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# Review on thermal energy storage with phase change materials and applications

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## Abstract

The use of a latent heat storage system using phase change materials (PCMs) is an effective way of storing thermal energy and has the advantages of high-energy storage density and the isothermal nature of the storage process. PCMs have been widely used in latent heat thermal-storage systems for heat pumps, solar engineering, and spacecraft thermal control applications. The uses of PCMs for heating and cooling applications for buildings have been investigated within the past decade. There are large numbers of PCMs that melt and solidify at a wide range of temperatures, making them attractive in a number of applications. This paper also summarizes the investigation and analysis of the available thermal energy storage systems incorporating PCMs for use in different applications.


*Keywords:* Thermal energy storage systems; Phase change material; Solar energy; Latent heat; Melt fraction

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## Nomenclature

| | |
|---|---|
| $a_m$ | fraction melted |
| $a_r$ | fraction reacted |
| $c$ | specific heat (J/kg °C) |
| $c_k$ | specific heat of phase $k$ in PCM (J/kg °C) |
| $C_{ap}$ | average specific heat between $T_i$ and $T_f$ (J/kg K) |
| $C_{lp}$ | average specific heat between $T_m$ and $T_f$ (J/kg K) |
| $C_p$ | specific heat (J/kg K) |
| $C_{sp}$ | average specific heat between $T_i$ and $T_m$ (kJ/kg K) |
| d$x$, $\Delta x$ | length of control volume (m) |
| d$y$, $\Delta y$ | height of control volume (m) |
| $f$ | melt fraction |
| $h$ | sensible volumetric enthalpy (J/m$^3$) |
| $\Delta h_m$ | heat of fusion per unit mass (J/kg) |
| $\Delta h_r$ | endothermic heat of reaction |
| $H$ | total volumetric enthalpy (J/m$^3$) |
| $k_k$ | thermal conductivity of phase $k$ in PCM (W/m °C) |
| $k_l$ | thermal conductivity of liquid phase (W/m °C) |
| $k_s$ | thermal conductivity of solid phase (W/m °C) |
| $L$ | length (m) |
| $m$ | mass of heat storage medium (kg) |
| $Q$ | quantity of heat stored (J) |
| $t$ | time (s) |
| $t^*$ | time (min) |
| $T$ | temperature (°C) |
| $T_f$ | final temperature (°C) |
| $T_i$ | initial temperature (°C) |
| $T_m$ | melting temperature (°C) |
| $X$, $x$ | space coordinate (m) |
| $Y$, $y$ | space coordinate (m) |

*Greek letters*

| | |
|---|---|
| $\alpha$ | thermal diffusivity of PCM (m$^2$/s) |
| $\alpha_f$ | thermal diffusivity of container material (m$^2$/s) |
| $\lambda$ | latent heat of fusion (J/kg) |
| $\rho$ | density (kg/m$^3$) |
| $\rho_k$ | density of phase $k$ in PCM (kg/m$^3$) |

*Subscript*

| | |
|---|---|
| f | heat exchanger container material |
| init | initial |
| l | liquid |
| m | melting |
| s | solid |
| wall | wall temperature |
| W, E, P, N, S | west, east, centre, north and south node |

*Superscript*

| | |
|---|---|
| $k$ | interaction level |
| o | old value |

## 1. Introduction

The continuous increase in the level of greenhouse gas emissions and the climb in fuel prices are the main driving forces behind efforts to more effectively utilize various sources of renewable energy. In many parts of the world, direct solar radiation is considered to be one of the most prospective sources of energy. The scientists all over the world are in search of new and renewable energy sources. One of the options is to develop energy storage devices, which are as important as developing new sources of energy. The storage of energy in suitable forms, which can conventionally be converted into the required form, is a present day challenge to the technologists. Energy storage not only reduces the mismatch between supply and demand but also improves the performance and reliability of energy systems and plays an important role in conserving the energy [1,2]. It leads to saving of premium fuels and makes the

system more cost effective by reducing the wastage of energy and capital cost. For example, storage would improve the performance of a power generation plant by load leveling and higher efficiency would lead to energy conservation and lesser generation cost. One of prospective techniques of storing thermal energy is the application of phase change materials (PCMs). Unfortunately, prior to the large-scale practical application of this technology, it is necessary to resolve numerous problems at the research and development stage. Types of energy storage methods are given below.

### 1.1. Energy storage methods

The different forms of energy that can be stored include mechanical, electrical and thermal energy [3].

#### 1.1.1. Mechanical energy storage

Mechanical energy storage systems include gravitational energy storage or pumped hydropower storage (PHPS), compressed air energy storage (CAES) and flywheels. The PHPS and CAES technologies can be used for large-scale utility energy storage while flywheels are more suitable for intermediate storage. Storage is carried out when inexpensive off-peak power is available, e.g., at night or weekends. The storage is discharged when power is needed because of insufficient supply from the base-load plant.

#### 1.1.2. Electrical storage

Energy storage through batteries is an option for storing the electrical energy. A battery is charged, by connecting it to a source of direct electric current and when it is discharged, the stored chemical energy is converted into electrical energy. Potential applications of batteries are utilization of off-peak power, load leveling, and storage of electrical energy generated by wind turbine or photovoltaic plants. The most common type of storage batteries is the lead acid and Ni–Cd.

#### 1.1.3. Thermal energy storage

Thermal energy storage can be stored as a change in internal energy of a material as sensible heat, latent heat and thermochemical or combination of these. An overview of major technique of storage of solar thermal energy is shown in Fig. 1 [4].

*1.1.3.1. Sensible heat storage.* In sensible heat storage (SHS), thermal energy is stored by raising the temperature of a solid or liquid. SHS system utilizes the heat capacity and the change in temperature of the material during the process of charging and discharging. The amount of heat stored depends on the specific heat of the medium, the temperature change and the amount of storage material [5].

$$Q = \int_{T_i}^{T_f} mC_p \, dT \tag{1}$$

$$= mC_{ap}(T_f - T_i) \tag{2}$$

The sensible heat storage capacity of some selected solid–liquid materials is shown in Table 1. Water appears to be the best SHS liquid available because it is inexpensive and has a high specific heat. However above 100 °C, oils, molten salts and liquid metals, etc. are used. For air heating applications rock bed type storage materials are used.

*1.1.3.2. Latent heat storage.* Latent heat storage (LHS) is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice versa. The storage capacity of the LHS system with a PCM medium [5] is given by

$$Q = \int_{T_i}^{T_m} mC_p \, dT + m a_m \Delta h_m + \int_{T_m}^{T_f} mC_p \, dT \tag{3}$$

$$Q = m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{lp}(T_f - T_m)] \tag{4}$$

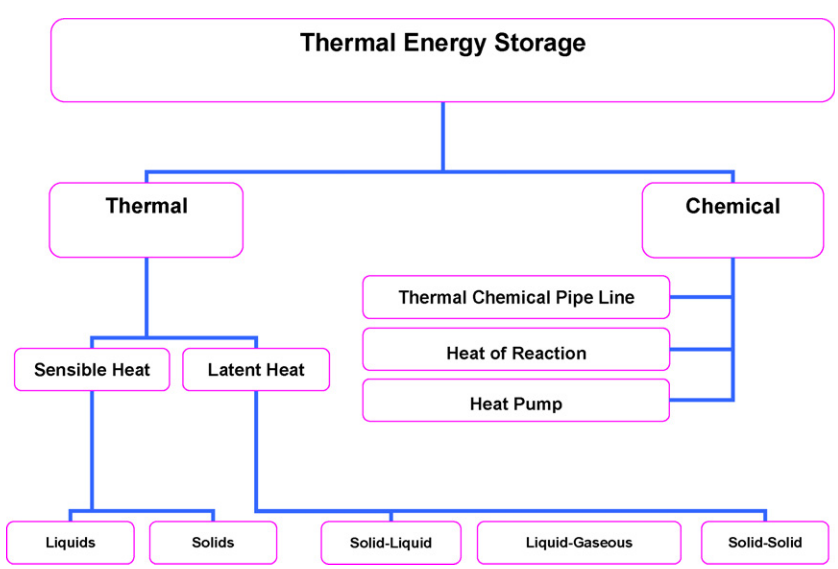



Fig. 1. Different types of thermal storage of solar energy.

Table 1
A list of selected solid–liquid materials for sensible heat storage

| Medium | Fluid type | Temperature range (°C) | Density ($kg/m^3$) | Specific heat (J/kg K) |
|---|---|---|---|---|
| Rock | | 20 | 2560 | 879 |
| Brick | | 20 | 1600 | 840 |
| Concrete | | 20 | 1900–2300 | 880 |
| Water | | 0–100 | 1000 | 4190 |
| Caloriea HT43 | Oil | 12–260 | 867 | 2200 |
| Engine oil | Oil | Up to 160 | 888 | 1880 |
| Ethanol | Organic liquid | Up to 78 | 790 | 2400 |
| Proponal | Organic liquid | Up to 97 | 800 | 2500 |
| Butanol | Organic liquid | Up to 118 | 809 | 2400 |
| Isotunaol | Organic liquid | Up to 100 | 808 | 3000 |
| Isopentanol | Organic liquid | Up to 148 | 831 | 2200 |
| Octane | Organic liquid | Up to 126 | 704 | 2400 |

#### *1.1.4. Thermochemical energy storage*

Thermochemical systems rely on the energy absorbed and released in breaking and reforming molecular bonds in a completely reversible chemical reaction. In this case, the heat stored depends on the amount of storage material, the endothermic heat of reaction, and the extent of conversion.

$$Q = a_r m \Delta h_r \quad (5)$$

Amongst above thermal heat storage techniques, latent heat thermal energy storage is particularly attractive due to its ability to provide high-energy storage density and its characteristics to store heat at constant temperature corresponding to the phase-transition temperature of phase change material (PCM). Phase change can be in the following form: solid–solid, solid–liquid, solid–gas, liquid–gas and vice versa.

In solid–solid transitions, heat is stored as the material is transformed from one crystalline to another. These transitions generally have small latent heat and small volume changes than solid–liquid transitions. Solid–solid PCMs offer the advantages of less stringent container requirements and greater design flexibility [6]. Most promising materials are organic solid solution of pentaerythritol (m.p. 188 °C, latent heat of fusion 323 kJ/kg), pentaglycerine (m.p. 81 °C, latent heat of fusion 216 kJ/kg), $Li_2SO_4$ (m.p. 578, latent heat of fusion 214 kJ/kg) and $KHF_2$ (m.p. 196 °C, latent heat of fusion 135 kJ/kg) [1]. Trombe wall with these materials could provide better performance than a plain concrete Trombe wall.

Solid–gas and liquid–gas transition through have higher latent heat of phase transition but their large volume changes on phase transition are associated with the containment problems and rule out their potential utility in thermal-storage systems. Large changes in volume make the system complex and impractical [7]. Solid–liquid transformations have comparatively smaller latent heat than liquid–gas. However, these transformations involve only a small change (of order of 10% or less) in volume. Solid–liquid transitions have proved to be economically attractive for use in thermal energy storage systems. PCMs themselves cannot be used as heat transfer medium. A separate heat transfer medium must me employed with heat exchanger in between to transfer energy from the source to the PCM and from PCM to the load. The heat exchanger to be used has to be designed specially, in view of the low thermal diffusivity of PCMs in general.

The volume changes of the PCMs on melting would also necessitate special volume design of the containers to wholes PCM. It should be able to absorb these volume changes and should also be compatible with the PCM used.

Any latent heat energy storage system therefore, possess at least following three components:

(i) a suitable PCM with its melting point in the desired temperature range,
(ii) a suitable heat exchange surface, and
(iii) a suitable container compatible with the PCM.

The development of a latent heat thermal energy storage system hence, involves the understanding of three essential subjects: phase change materials, containers materials and heat exchangers. A wide range of technical options available for storing low temperature thermal energy is shown in Fig. 2 [7].

## 2. Latent heat storage materials

Phase change materials (PCM) are ‘‘Latent’’ heat storage materials. The thermal energy transfer occurs when a material changes from solid to liquid, or liquid to solid. This is called a change in state, or ‘‘Phase.’’ Initially, these solid–liquid PCMs perform like conventional storage materials, their temperature rises as they absorb heat. Unlike conventional (sensible) storage materials, PCM absorbs and release heat at a nearly constant temperature. They store 5–14 times more heat per unit volume than sensible storage materials such as water, masonry, or rock. A large number of PCMs are known to melt with a heat of fusion in any required range. However, for their employment as latent heat storage materials these materials must exhibit certain desirable thermodynamic, kinetic and chemical properties. Moreover, economic considerations and easy availability of these materials has to be kept in mind.

The PCM to be used in the design of thermal-storage systems should passes desirable thermophysical, kinetics and chemical properties which are as follows [8,9]:

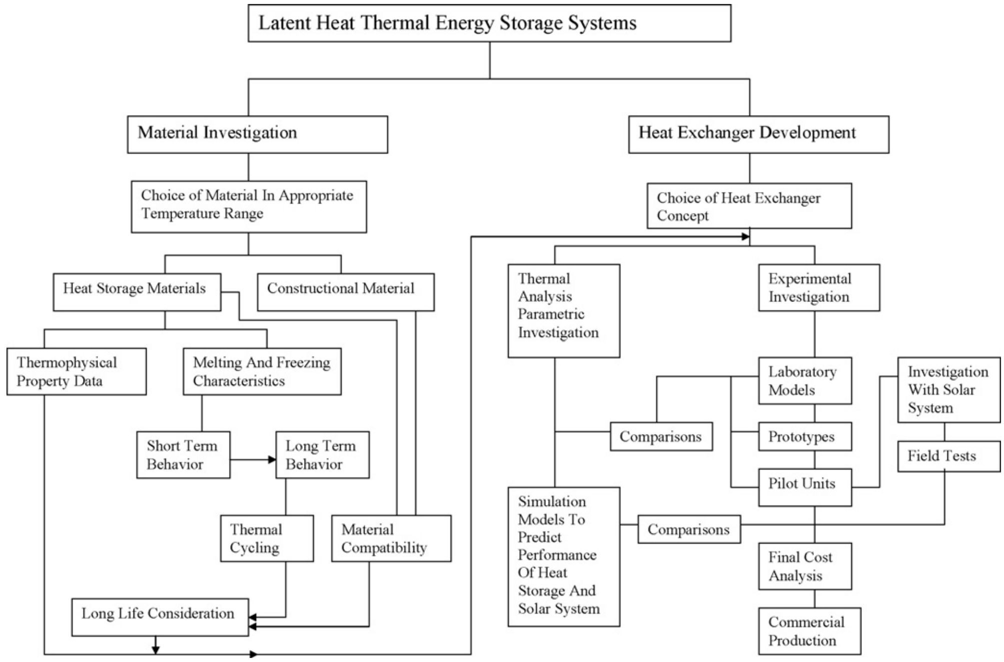



Fig. 2. Flow chart showing different stages involved in the development of a latent heat storage system.

### 2.1. Thermal properties

(i) Suitable phase-transition temperature.
(ii) High latent heat of transition.
(iii) Good heat transfer.

Selecting a PCM for a particular application, the operating temperature of the heating or cooling should be matched to the transition temperature of the PCM. The latent heat should be as high as possible, especially on a volumetric basis, to minimize the physical size of the heat store. High thermal conductivity would assist the charging and discharging of the energy storage.

### 2.2. Physical properties

(i) Favorable phase equilibrium.
(ii) High density.
(iii) Small volume change.
(iv) Low vapor pressure.

Phase stability during freezing melting would help towards setting heat storage and high density is desirable to allow a smaller size of storage container. Small volume changes on phase transformation and small vapor pressure at operating temperatures to reduce the containment problem.

### 2.3. Kinetic properties

(i) No supercooling.
(ii) Sufficient crystallization rate.

Supercooling has been a troublesome aspect of PCM development, particularly for salt hydrates. Supercooling of more than a few degrees will interfere with proper heat extraction from the store, and 5–10 °C supercooling can prevent it entirely.

### 2.4. Chemical properties

(i) Long-term chemical stability.
(ii) Compatibility with materials of construction.
(iii) No toxicity.
(iv) No fire hazard.

PCM can suffer from degradation by loss of water of hydration, chemical decomposition or incompatibility with materials of construction. PCMs should be non-toxic, non-flammable and non-explosive for safety.

### 2.5. Economics

(i) Abundant.
(ii) Available.
(iii) Cost effective.

Low cost and large-scale availability of the phase change materials is also very important.

## 3. Classification of PCMs

A large number of phase change materials (organic, inorganic and eutectic) are available in any required temperature range. A classification of PCMs is given in Fig. 3.

There are a large number of organic and inorganic chemical materials, which can be identified as PCM from the point of view melting temperature and latent heat of fusion. However, except for the melting point in the operating range, majority of phase change materials does not satisfy the criteria required for

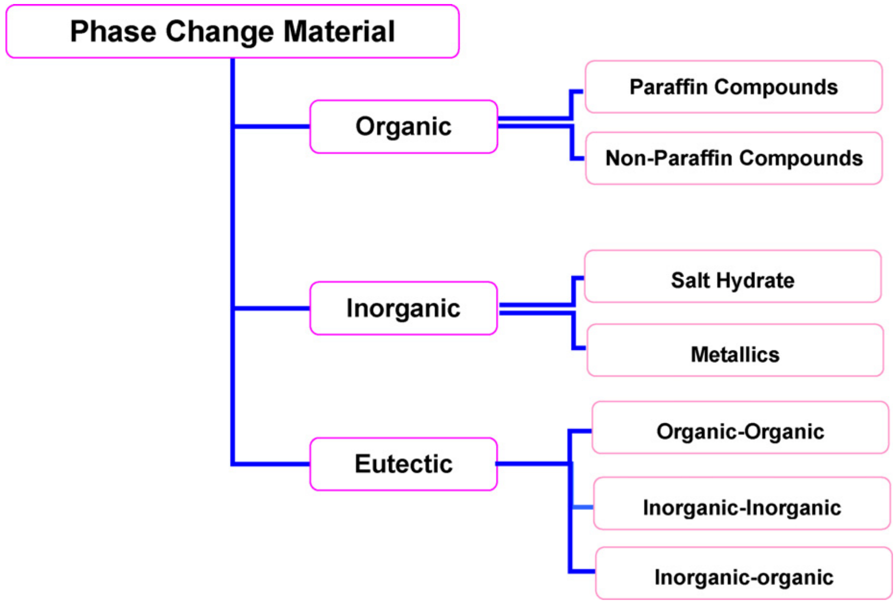



Fig. 3. Classification of PCMs.

an adequate storage media as discussed earlier. As no single material can have all the required properties for an ideal thermal-storage media, one has to use the available materials and try to make up for the poor physical property by an adequate system design. For example metallic fins can be used to increase the thermal conductivity of PCMs, supercooling may be suppressed by introducing a nucleating agent or a 'cold finger' in the storage material and incongruent melting can be inhibited by use of suitable thickness.

In general inorganic compounds have almost double volumetric latent heat storage capacity (250–400 kg/dm$^3$) than the organic compounds (128–200 kg/dm$^3$). For their very different thermal and chemical behavior, the properties of each subgroup which affects the design of latent heat thermal energy storage systems using PCMs of that subgroup are discussed in detail below.

### 3.1. Organic phase change materials

Organic materials are further described as paraffin and non-paraffins. Organic materials include congruent melting means melt and freeze repeatedly without phase segregation and consequent degradation of their latent heat of fusion, self nucleation means they crystallize with little or no supercooling and usually non-corrosiveness.

#### 3.1.1. Paraffins

Paraffin wax consists of a mixture of mostly straight chain *n*-alkanes $CH_3$–$(CH_2)$–$CH_3$. The crystallization of the $(CH_3)$-chain release a large amount of latent heat. Both the melting point and latent heat of fusion increase with chain length. Paraffin qualifies as heat of fusion storage materials due to their availability in a large temperature range. Due to cost consideration, however, only technical grade paraffins may be used as PCMs in latent heat storage systems. Paraffin is safe, reliable, predictable, less expensive and non-corrosive. They are chemically inert and stable below 500 °C, show little volume changes on melting and have low vapor pressure in the melt form. For these properties of the paraffins, system-using paraffins usually have very long freeze–melt cycle. Table 2a lists thermal properties of some technical grade paraffins, which are essentially, paraffin mixtures and are not completely refined oil [10]. The melting point of alkane increases with the increasing number of carbon atoms. Apart from some several favorable characteristic of paraffins, such as congruent melting and good nucleating properties. They show some undesirable properties such as: (i) low thermal conductivity, (ii) non-compatible with the plastic container and (iii) moderately flammable. All these undesirable effects can be partly eliminated by slightly modifying the wax and the storage unit. Some selected paraffins are shown in Table 2b along-with their melting point, latent heat of fusion and groups. PCMs are categorized as: (i) group I, most promising; (ii) group II, promising; and (iii) group III, less promising.

Table 2a
Physical properties of some paraffin's

| Paraffin[a] | Freezing point/ range (°C) | Heat of fusion (kJ/kg) | Group[b] |
|---|---|---|---|
| 6106 | 42–44 | 189 | I |
| P116[c] | 45–48 | 210 | I |
| 5838 | 48–50 | 189 | I |
| 6035 | 58–60 | 189 | I |
| 6403 | 62–64 | 189 | I |
| 6499 | 66–68 | 189 | I |

[a] Manufacturer of technical Grade Paraffin's 6106, 5838, 6035, 6403 and 6499: Ter Hell Paraffin Hamburg, FRG.
[b] Group I, most promising; group II, promising; group III, less promising; — insufficient data.
[c] Manufacturer of Paraffin's P116: Sun Company, USA.

Table 2b
Melting point and latent heat of fusion: paraffins

| No. of carbon atoms | Melting point (°C) | Latent heat of fusion (kJ/kg) | Group[a] |
|---|---|---|---|
| 14 | 5.5 | 228 | I |
| 15 | 10 | 205 | II |
| 16 | 16.7 | 237.1 | I |
| 17 | 21.7 | 213 | II |
| 18 | 28.0 | 244 | I |
| 19 | 32.0 | 222 | II |
| 20 | 36.7 | 246 | I |
| 21 | 40.2 | 200 | II |
| 22 | 44.0 | 249 | II |
| 23 | 47.5 | 232 | II |
| 24 | 50.6 | 255 | II |
| 25 | 49.4 | 238 | II |
| 26 | 56.3 | 256 | II |
| 27 | 58.8 | 236 | II |
| 28 | 61.6 | 253 | II |
| 29 | 63.4 | 240 | II |
| 30 | 65.4 | 251 | II |
| 31 | 68.0 | 242 | II |
| 32 | 69.5 | 170 | II |
| 33 | 73.9 | 268 | II |
| 34 | 75.9 | 269 | II |

[a] Group I, most promising; group II, promising; group III, less promising; — insufficient data.

### 3.1.2. Non-paraffins

The non-paraffin organic are the most numerous of the phase change materials with highly varied properties. Each of these materials will have its own properties unlike the paraffin's, which have very similar properties. This is the largest category of candidate's materials for phase change storage. Abhat et al. [11] and Buddhi and Sawhney [9] have conducted an extensive survey of organic materials and identified a number of esters, fatty acids, alcohol's and glycol's suitable for energy storage. These organic materials are further subgroups as fatty acids and other non-paraffin organic. These materials are flammable and should not be exposed to excessively high temperature, flames or oxidizing agents. Few non-paraffin's are tabulated in Table 3.

Some of the features of these organic materials are as follows: (i) high heat of fusion, (ii) inflammability, (iii) low thermal conductivity, (iv) low flash points, (v) varying level of toxicity, and (vi) instability at high temperatures.

Fatty acids have high heat of fusion values comparable to that of paraffin's. Fatty acids also show reproducible melting and freezing behavior and freeze with no supercooling [12,13]. The general formula describing all the fatty acid is given by $CH_3(CH_2)_{2n}{\cdot}COOH$ and hence, qualify as good PCMs. Their major drawback, however, is their cost, which are 2–2.5 times greater than that of technical grade paraffin's. They are also mild corrosive. Some fatty acids of interest to low temperature latent heat thermal energy storage applications and are tabulated in Table 4.

### 3.2. Inorganic phase change materials

Inorganic materials are further classified as salt hydrate and metallics. These phase change materials do not supercool

Table 3
Melting point and latent heat of fusion: non paraffins

| Material | Melting point (°C) | Latent heat (kJ/kg) | Group[a] |
|---|---|---|---|
| Formic acid | 7.8 | 247 | III |
| Caprilic acid | 16.3 | 149 | – |
| Glycerin | 17.9 | 198.7 | III |
| D-Lattic acid | 26 | 184 | I |
| Methyl palmitate | 29 | 205 | II |
| Camphenilone | 39 | 205 | II |
| Docasyl bromide | 40 | 201 | II |
| Caprylone | 40 | 259 | II |
| Phenol | 41 | 120 | III |
| Heptadecanone | 41 | 201 | II |
| 1-Cyclohexylooctadecane | 41 | 218 | II |
| 4-Heptadacanone | 41 | 197 | II |
| *p*-Joluidine | 43.3 | 167 | – |
| Cyanamide | 44 | 209 | II |
| Methyl eicosanate | 45 | 230 | II |
| 3-Heptadecanone | 48 | 218 | II |
| 2-Heptadecanone | 48 | 218 | II |
| Hydrocinnamic acid | 48.0 | 118 | – |
| Cetyl alcohol | 49.3 | 141 | – |
| α-Nepthylamine | 50.0 | 93 | – |
| Camphene | 50 | 238 | III |
| *O*-Nitroaniline | 50.0 | 93 | – |
| 9-Heptadecanone | 51 | 213 | II |
| Thymol | 51.5 | 115 | – |
| Methyl behenate | 52 | 234 | II |
| Diphenyl amine | 52.9 | 107 | – |
| *p*-Dichlorobenzene | 53.1 | 121 | – |
| Oxolate | 54.3 | 178 | – |
| Hypophosphoric acid | 55 | 213 | II |
| *O*-Xylene dichloride | 55.0 | 121 | – |
| β-Chloroacetic acid | 56.0 | 147 | III |
| Chloroacetic acid | 56 | 130 | III |
| Nitro naphthalene | 56.7 | 103 | – |
| Trimyristin | 33–57 | 201–213 | I |
| Heptaudecanoic acid | 60.6 | 189 | II |
| α-Chloroacetic acid | 61.2 | 130 | – |
| Bee wax | 61.8 | 177 | II |
| Bees wax | 61.8 | 177 | II |
| Glyolic acid | 63.0 | 109 | – |
| Glycolic acid | 63 | 109 | – |
| *p*-Bromophenol | 63.5 | 86 | – |
| Azobenzene | 67.1 | 121 | – |
| Acrylic acid | 68.0 | 115 | – |
| Dinto toluent (2,4) | 70.0 | 111 | – |
| Phenylacetic acid | 76.7 | 102 | – |
| Thiosinamine | 77.0 | 140 | – |
| Bromcamphor | 77 | 174 | – |
| Durene | 79.3 | 156 | – |
| Benzylamine | 78.0 | 174 | – |
| Methyl brombrenzoate | 81 | 126 | – |
| Alpha napthol | 96 | 163 | – |
| Glautaric acid | 97.5 | 156 | – |
| *p*-Xylene dichloride | 100 | 138.7 | – |
| Catechol | 104.3 | 207 | III |
| Quinone | 115 | 171 | II |
| Acetanilide | 118.9 | 222 | II |
| Succinic anhydride | 119 | 204 | II |
| Benzoic acid | 121.7 | 142.8 | III |
| Stibene | 124 | 167 | – |
| Benzamide | 127.2 | 169.4 | III |

[a] Group I, most promising; group II, promising; group III, Less promising; — insufficient data.

Table 4
Melting point and latent heat of fusion: fatty acids

| Material | Formula | Melting point (°C) | Latent heat (kJ/kg) | Group[a] |
|---|---|---|---|---|
| Acetic acid | $CH_3COOH$ | 16.7 | 184 | I |
| Polyethylene glycol 600 | $H(OC_2H_2)_n \cdot OH$ | 20–25 | 146 | I |
| Capric acid | $CH_3(CH_2)_8 \cdot COOH$ | 36 | 152 | – |
| Eladic acid | $C_8H_7C_9H_{16} \cdot COOH$ | 47 | 218 | I |
| Lauric acid | $CH_3(CH_2)_{10} \cdot COOH$ | 49 | 178 | II |
| Pentadecanoic acid | $CH_3(CH_2)_{13} \cdot COOH$ | 52.5 | 178 | – |
| Tristearin | $(C_{17}H_{35}COO)C_3H_5$ | 56 | 191 | I |
| Myristic acid | $CH_3(CH_2)_{12} \cdot COOH$ | 58 | 199 | I |
| Palmatic acid | $CH_3(CH_2)_{14} \cdot COOH$ | 55 | 163 | I |
| Stearic acid | $CH_3(CH_2)_{16} \cdot COOH$ | 69.4 | 199 | I |
| Acetamide | $CH_3CONH_2$ | 81 | 241 | I |
| Methyl fumarate | $(CHCO_2NH_3)_2$ | 102 | 242 | I |

[a] Group I, most promising; group II, promising; group III, less promising; —insufficient data.

appreciably and their heats of fusion do not degrade with cycling.

### 3.2.1. *Salt hydrates*

Salt hydrates may be regarded as alloys of inorganic salts and water forming a typical crystalline solid of general formula $AB \cdot nH_2O$. The solid–liquid transformation of salt hydrates is actually a dehydration of hydration of the salt, although this process resembles melting or freezing thermodynamically. A salt hydrates usually melts to either to a salt hydrate with fewer moles of water, i.e.

$$AB \cdot nH_2O \rightarrow AB \cdot mH_2O + (n-m)H_2O \tag{6}$$

or to its anhydrous form

$$AB \cdot nH_2O \rightarrow AB + nH_2O \tag{7}$$

At the melting point the hydrate crystals breakup into anhydrous salt and water, or into a lower hydrate and water. One problem with most salt hydrates is that of incongruent melting caused by the fact that the released water of crystallization is not sufficient to dissolve all the solid phase present. Due to density difference, the lower hydrate (or anhydrous salt) settles down at the bottom of the container.

Most salt hydrates also have poor nucleating properties resulting in supercooling of the liquid before crystallization beings. One solution to this problem is to add a nucleating agent, which provides the nucleion which crystal formation is initiated. Another possibility is to retain some crystals, in a small cold region, to serve as nuclei.

Salt hydrates are the most important group of PCMs, which have been extensively studied for their use in latent heat thermal energy storage systems. The most attractive properties of salt hydrates are: (i) high latent heat of fusion per unit volume, (ii) relatively high thermal conductivity (almost double of the paraffin's), and (iii) small volume changes on melting. They are not very corrosive, compatible with plastics and only slightly toxic. Many salt hydrates are sufficiently inexpensive for the use in storage [14].

Three types of the behavior of the melted salts can be identified: congruent, incongruent and semi-congruent melting.

(i) Congruent melting occurs when the anhydrous salt is completely soluble in its water of hydration at the melting temperature.
(ii) Incongruent melting occurs when the salt is not entirely soluble in its water of hydration at the melting point.
(iii) Semi-congruent melting the liquid and solid phases in equilibrium during a phase transition is of different melting composition because of conversion of the hydrate to a lower-hydrated material through loss of water.

The major problem in using salt hydrates, as PCMs is the most of them, which are judged suitable for use in thermal storage, melts incongruently. As $n$ moles of water of hydration are not sufficient to dissolves one mole of salt, the resulting solution is supersaturated at the melting temperature. The solid salt, due to its higher density, settles down at the bottom of the container and is unavailable for recombination with water during the reverse process of freezing. This results in an irreversible melting–freezing of the salt hydrate goes on decreasing with each charge–discharge cycle.

Another important problem common to salt hydrates is that of supercooling. At the fusion temperature, the rate of nucleation is generally very low. To achieve a reasonable rate of nucleation, the solution has to be supercooled and hence energy instead of being discharged at fusion temperature is discharged at much lower temperature.

Other problem faced with salt hydrates is the spontaneous of salt hydrates with lower number of water moles during the discharge process. Adding chemicals can prevent the nucleation of lower salt hydrates, which preferentially increases the solubility of lower salt hydrates over the original salt hydrates with higher number of water moles.

The problem of incongruent melting can be tackled by one of the following means: (i) by mechanical stirring [14], (ii) by encapsulating the PCM to reduce separation [15], (iii) by adding of the thickening agents which prevent setting of the solid salts by holding it in suspension [16], (iv) by use of excess of water so that melted crystals do not produce supersaturated solution [17], (v) by modifying the chemical composition of the system and making incongruent material congruent [18,19].

To overcome the problem of salt segregation and supercooling of salt hydrates, scientists of General Electric Co., NY [20] suggested a rolling cylinder heat storage system. The system consists of a cylindrical vessel mounted horizontally with two sets of rollers. A rotation rate of 3 rpm produced sufficient motion of the solid content (i) to create effective chemical equilibrium, (ii) to prevent nucleation of solid crystals on the walls, and (iii) to assume rapid attainment of axial equilibrium in long cylinders. Some of the advantages of the rolling cylinder method as listed by Herrick et al. [21] are: (i) complete phase change, (ii) latent heat released was in the range of 90–100% of the theoretical latent heat, (iii) repeatable performance over 200 cycles, (iv) high internal heat transfer rates, (v) freezing occurred uniformly. A list of salt hydrates is given in Table 5.

Table 5
Melting point and latent heat of fusion: salt hydrates

| Material | Melting point (°C) | Latent heat (kJ/kg) | Group[a] |
|---|---|---|---|
| $K_2HPO_4{\cdot}6H_2O$ | 14.0 | 109 | II |
| $FeBr_3{\cdot}6H_2O$ | 21.0 | 105 | II |
| $Mn(NO_3)_2{\cdot}6H_2O$ | 25.5 | 148 | II |
| $FeBr_3{\cdot}6H_2O$ | 27.0 | 105 | II |
| $CaCl_2{\cdot}12H_2O$ | 29.8 | 174 | I |
| $LiNO_3{\cdot}2H_2O$ | 30.0 | 296 | I |
| $LiNO_3{\cdot}3H_2O$ | 30 | 189 | I |
| $Na_2CO_3{\cdot}10H_2O$ | 32.0 | 267 | II |
| $Na_2SO_4{\cdot}10H_2O$ | 32.4 | 241 | II |
| $KFe(SO_4)_2{\cdot}12H_2O$ | 33 | 173 | I |
| $CaBr_2{\cdot}6H_2O$ | 34 | 138 | II |
| $LiBr_2{\cdot}2H_2O$ | 34 | 124 | I |
| $Zn(NO_3)_2{\cdot}6H_2O$ | 36.1 | 134 | III |
| $FeCl_3{\cdot}6H_2O$ | 37.0 | 223 | I |
| $Mn(NO_3)_2{\cdot}4H_2O$ | 37.1 | 115 | II |
| $Na_2HPO_4{\cdot}12H_2O$ | 40.0 | 279 | II |
| $CoSO_4{\cdot}7H_2O$ | 40.7 | 170 | I |
| $KF{\cdot}2H_2O$ | 42 | 162 | III |
| $MgI_2{\cdot}8H_2O$ | 42 | 133 | III |
| $CaI_2{\cdot}6H_2O$ | 42 | 162 | III |
| $K_2HPO_4{\cdot}7H_2O$ | 45.0 | 145 | II |
| $Zn(NO_3)_2{\cdot}4H_2O$ | 45 | 110 | III |
| $Mg(NO_3){\cdot}4H_2O$ | 47.0 | 142 | II |
| $Ca(NO_3){\cdot}4H_2O$ | 47.0 | 153 | I |
| $Fe(NO_3)_3{\cdot}9H_2O$ | 47 | 155 | I |
| $Na_2SiO_3{\cdot}4H_2O$ | 48 | 168 | II |
| $K_2HPO_4{\cdot}3H_2O$ | 48 | 99 | II |
| $Na_2S_2O_3{\cdot}5H_2O$ | 48.5 | 210 | II |
| $MgSO_4{\cdot}7H_2O$ | 48.5 | 202 | II |
| $Ca(NO_3)_2{\cdot}3H_2O$ | 51 | 104 | I |
| $Zn(NO_3)_2{\cdot}2H_2O$ | 55 | 68 | III |
| $FeCl_3{\cdot}2H_2O$ | 56 | 90 | I |
| $Ni(NO_3)_2{\cdot}6H_2O$ | 57.0 | 169 | II |
| $MnCl_2{\cdot}4H_2O$ | 58.0 | 151 | II |
| $MgCl_2{\cdot}4H_2O$ | 58.0 | 178 | II |
| $CH_3COONa{\cdot}3H_2O$ | 58.0 | 265 | II |
| $Fe(NO_3)_2{\cdot}6H_2O$ | 60.5 | 126 | – |
| $NaAl(SO_4)_2{\cdot}10H_2O$ | 61.0 | 181 | I |
| $NaOH{\cdot}H_2O$ | 64.3 | 273 | I |
| $Na_3PO_4{\cdot}12H_2O$ | 65.0 | 190 | – |
| $LiCH_3COO{\cdot}2H_2O$ | 70 | 150 | II |
| $Al(NO_3)_2{\cdot}9H_2O$ | 72 | 155 | I |
| $Ba(OH)_2{\cdot}8H_2O$ | 78 | 265 | II |
| $Mg(NO_3)_2{\cdot}6H_2O$ | 89.9 | 167 | II |
| $KAl\ (SO_4)_2{\cdot}12H_2O$ | 91 | 184 | II |
| $MgCl_2{\cdot}6H_2O$ | 117 | 167 | I |

[a] Group I, most promising; group II, promising; group III, less promising; — insufficient data.

### 3.2.2. Metallics

This category includes the low melting metals and metal eutectics. These metallics have not yet been seriously considered for PCM technology because of weight penalties. However, when volume is a consideration, they are likely candidates because of the high heat of fusion per unit volume. They have high thermal conductivities, so fillers with added weight penalties are not required. The use of metallics poses a number of unusual engineering problems. A major difference between the metallics and other PCMs is their high thermal conductivity. A list of some selected metallics is given in Table 6.

Some of the features of these materials are as follows: (i) low heat of fusion per unit weight (ii) high heat of fusion per unit volume, (iii) high thermal conductivity, (iv) low specific heat and (v) relatively low vapor pressure.

## 3.3. Eutectics

A eutectic is a minimum-melting composition of two or more components, each of which melts and freeze congruently forming a mixture of the component crystals during crystallization [22]. Eutectic nearly always melts and freezes without segregation since they freeze to an intimate mixture of crystals, leaving little opportunity for the components to separate. On melting both components liquefy simultaneously, again with separation unlikely.

Some segregation PCM compositions have sometimes been incorrectly called eutectics, since they are minimum melting. Because of the components undergoes a peritectic reaction during phase transition, however, they should more properly be termed peritectics. Freezing point of the mixture of tetradecane (m.p. 5.3 °C) and hexadedane (m.p. 17.9 °C) is shown in Fig. 4 [23]. The eutectic point of laboratory grade hexadecane–tetradecane mixture occurs at approximately 91.67% of

Table 6
Melting point and latent heat of fusion: metallics

| Material | Melting point (°C) | Latent heat (kJ/kg) | Group[a] |
|---|---|---|---|
| Gallium–gallium antimony eutectic | 29.8 | – | – |
| Gallium | 30.0 | 80.3 | I |
| Cerrolow eutectic | 58 | 90.9 | – |
| Bi–Cd–In eutectic | 61 | 25 | – |
| Cerrobend eutectic | 70 | 32.6 | I |
| Bi–Pb–In eutectic | 70 | 29 | – |
| Bi–In eutectic | 72 | 25 | – |
| Bi–Pb–tin eutectic | 96 | – | – |
| Bi–Pb eutectic | 125 | – | – |

[a] Group I, most promising; group II, promising; group III, less promising; — insufficient data.

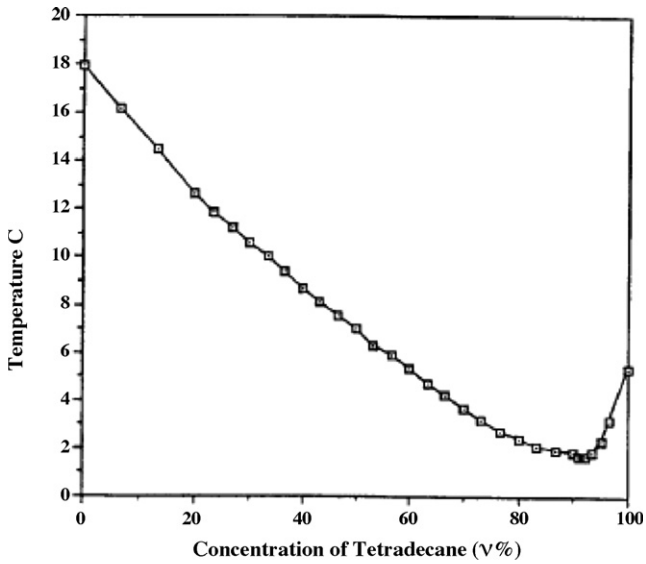



Fig. 4. Freezing point of the mixture of tetradecane and hexadecane.

tetradecane, and its phase change temperature is approximately 1.7 °C. A list of eutectic is given in Table 7.

## 4. Measurement techniques of latent heat of fusion and melting temperature

The techniques presently used for latent heat of fusion and melting temperature of PCMs are: (i) differential thermal analysis (DTA), and (ii) differential scanning calorimeter (DSC). [24]. In DSC and DTA techniques, sample and reference materials are heated at constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials and the record is the DSC curve. The recommended reference material is alumina ($Al_2O_3$). Latent heat of fusion is calculated using the area under the peak and melting temperature is estimated by the tangent at the point of greatest slope on the face portion of the peak.

## 5. Thermal energy storage systems: a review

### 5.1. Solar water-heating systems

Solar water heater is getting popularity [25,26] since they are relatively inexpensive and simple to fabricate and maintain. Prakesh et al. [27] analyzed a built in storage type water heater containing a layer of PCM filled at the bottom. During the sunshine hours, the water gets heated up which in turn transfers heat to the PCM below it. The PCM collects energy in the form of latent heat and melts. During off sunshine hours, the hot water is withdrawn and is substituted by cold water, which gains energy from the PCM. The energy is released by the PCM on changing its phases from liquid to solid. This type of system may not be effective due to the poor heat transfer between PCM and water. A cylindrical storage unit in the closed loop with a flat plate collector has been theoretically studied by Bansal and Buddhi [28] for its charging and discharging mode. The calculations for the interface moving boundary and fluid temperature were made by using paraffin wax (p-116) and stearic acid as phase change materials. A comparative study of solar energy storage systems based on the latent heat and sensible heat technique has been carried out to preserve the solar heated hot water for night duration by Chaurasia et al. [29]. For this purpose, two identical storage units were used. One storage unit contained 17.5 kg paraffin wax (m.p. about 54 °C) as the storage material packed in a heat exchanger made of the aluminum tubes and another unit simply contained the water as a storage material in a GI tank. Both units were

Table 7
List of organic and inorganic eutectics

| Material | Composition (wt.%) | Melting point (°C) | Latent heat (kJ/kg) | Group[a] |
|---|---|---|---|---|
| $CaCl_2{\cdot}6H_2O + CaBr_2{\cdot}6H_2O$ | 45 + 55 | 14.7 | 140 | – |
| Triethylolethane + water + urea | 38.5 + 31.5 + 30 | 13.4 | 160 | I |
| $C_{14}H_{28}O_2 + C_{10}H_{20}O_2$ | 34 + 66 | 24 | 147.7 | – |
| $CaCl_2 + MgCl_2{\cdot}6H_2O$ | 50 + 50 | 25 | 95 | II |
| $CH_3CONH_2 + NH_2CONH_2$ | 50 + 50 | 27 | 163 | II |
| Triethylolethane + urea | 62.5 + 37.5 | 29.8 | 218 | I |
| $Ca(NO_3){\cdot}4H_2O + Mg(NO_3)_3{\cdot}6H_2O$ | 47 + 53 | 30 | 136 | – |
| $CH_3COONa{\cdot}3H_2O + NH_2CONH_2$ | 40 + 60 | 30 | 200.5 | I |
| $NH_2CONH_2 + NH_4NO_3$ | 53 + 47 | 46 | 95 | II |
| $Mg(NO_3)_3{\cdot}6H_2O + NH_4NO_3$ | 61.5 + 38.5 | 52 | 125.5 | I |
| $Mg(NO_3)_3{\cdot}6H_2O + MgCl_2{\cdot}6H_2O$ | 58.7 + 41.3 | 59 | 132.2 | I |
| $Mg(NO_3)_3{\cdot}6H_2O + MgCl_2{\cdot}6H_2O$ | 50 + 50 | 59.1 | 144 | – |
| $Mg(NO_3)_3{\cdot}6H_2O + Al(NO_3)_2{\cdot}9H_2O$ | 53 + 47 | 61 | 148 | – |
| $CH_3CONH_2 + C_{17}H_{35}COOH$ | 50 + 50 | 65 | 218 | – |
| $Mg(NO_3)_2{\cdot}6H_2O + MgBr_2{\cdot}6H_2O$ | 59 + 41 | 66 | 168 | I |
| Napthalene + benzoic acid | 67.1 + 32.9 | 67 | 123.4 | – |
| $NH_2CONH_2 + NH_4Br$ | 66.6 + 33.4 | 76 | 151 | II |
| $LiNO_3 + NH_4NO_3 + NaNO_3$ | 25 + 65 + 10 | 80.5 | 113 | – |
| $LiNO_3 + NH_4NO_3 + KNO_3$ | 26.4 + 58.7 + 14.9 | 81.5 | 116 | – |
| $LiNO_3 + NH_4NO_3 + NH_4Cl$ | 27 + 68 + 5 | 81.6 | 108 | – |

[a] Group I, most promising; group II, promising; group III, less promising; —insufficient data.

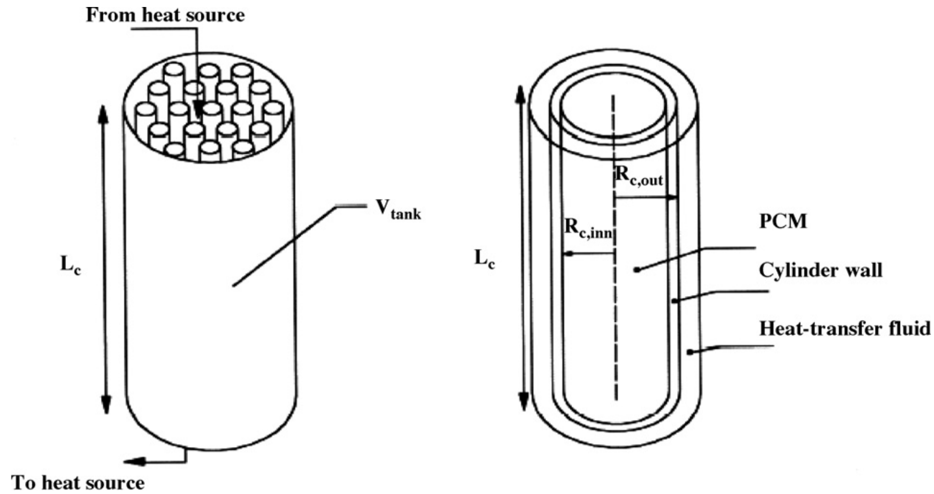



Fig. 5. A cylindrical shell with PCM storage.

separately charged during the day with the help of the flat plate solar collectors having same absorbing area. This study has revealed that the latent heat storage system comparatively yields more hot water on the next day morning as compared to sensible storage system.

A comparison has been made between different sized latent heat storage vessels and sensible heat storage in a water tank with different degree of stratification [30]. The storage vessel consists of a number of closed cylindrical pipes filled with the phase change medium (Fig. 5). These pipes were surrounded by heat transfer fluid. Bajnoczy et al. [31] studied the two-grade heat storage system (60–30 °C and 30–20 °C) based on calcium chloride hexahydrate and calcium chloride tetrahydrate. Authors also studied the storage capacity changes during the cycles and possible use of a solar energy storage system for domestic water-heating system. Kamiz Kayguz et al. [32] had conducted an experimental and theoretical study to determine the performance of phase change energy storage materials for solar water-heating systems. $CaCl_2{\cdot}6H_2O$ was used as phase change material. Author also compared the performance of PCM, water and rock based storage system (Fig. 6). Whenever solar energy is available, it is collected and transferred to the energy storage tank that is filled by 1500 kg encapsulated phase change material (PCM). It consisted of a vessel packed in the horizontal direction with cylindrical tubes. The energy storage material ($CaCl_2{\cdot}6H_2O$) is inside the tubes (the tube container made of PVC plastic) and heats transfer fluid (water) flow parallel to them. Rabin et al. [33] also studied a solar collector with storage for water heating having salt hydrate as a phase change material. The results of parametric studies on the effect of the transition temperature and of the thickness layer of the salt-hydrate PCM on the thermal performance of the charging process are also presented. Sharma et al. [34] designed, developed and performance evaluate of a latent heat storage unit for evening and morning hot water requirements, using a box type solar collector. Paraffin wax (m.p. 54 °C) was used as a latent heat storage material and found that the performance of the latent heat storage unit in the system was very good to get the hot water in the desirable temperature range.

Mettawee and Assassa [35] investigated a the thermal performance of a compact phase change material (PCM) solar collector based on latent heat storage. In this collector, the absorber plate–container unit performs the function of both absorbing the solar energy and storing PCM. The solar energy was stored in paraffin wax, which was used as a PCM, and was discharged to cold water flowing in pipes located inside the

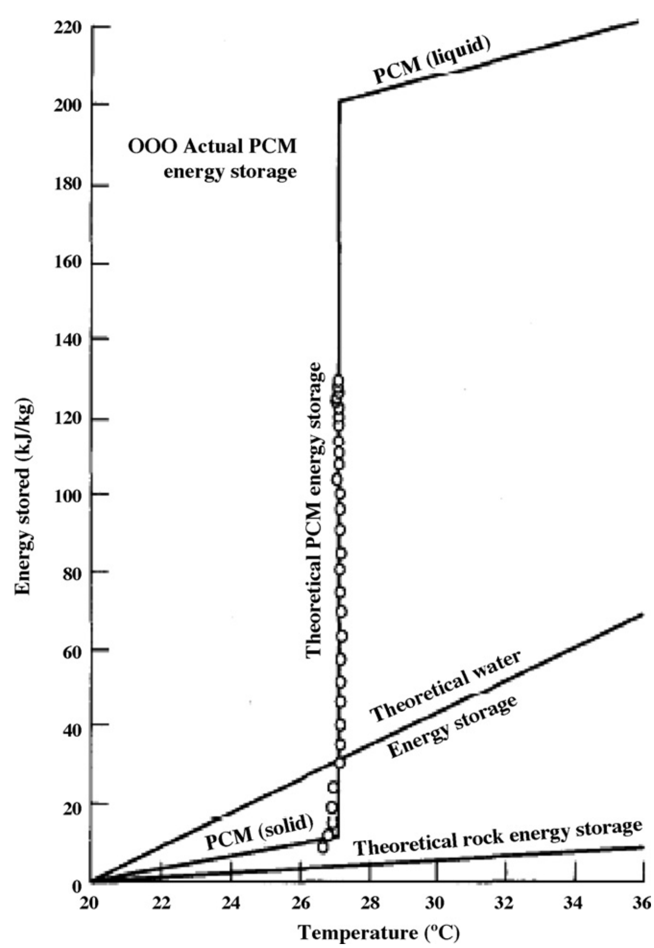



Fig. 6. Performance comparison of PCM, water and rock storage system.

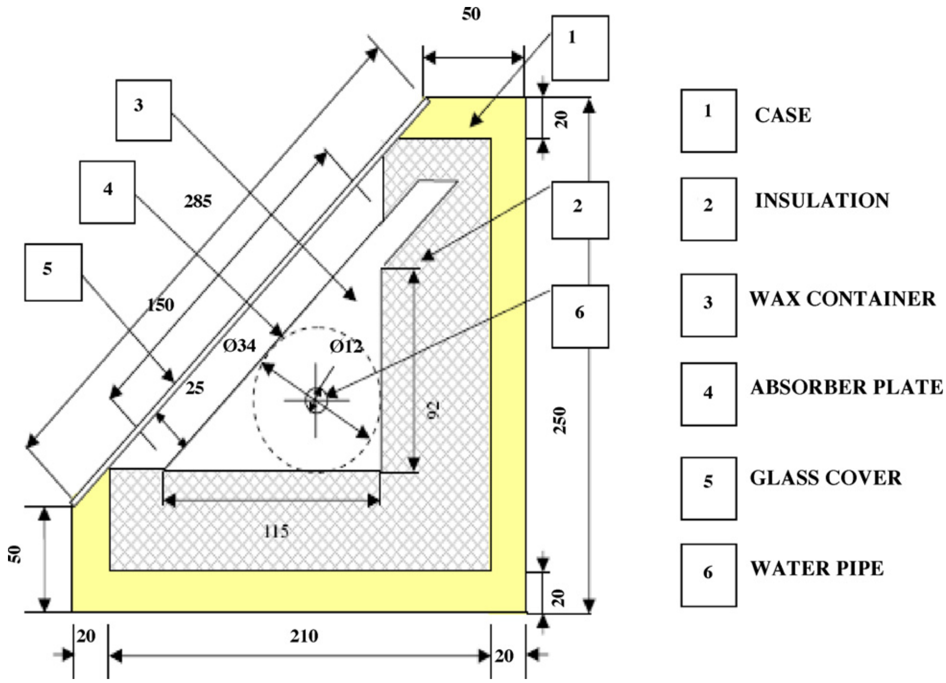



Fig. 7. Schematic of the experimental apparatus cross-section.

wax. The collector's effective area was assumed to be 1 $m^2$ and its total volume was divided into five sectors. The experimental apparatus was designed to simulate one of the collector's sectors, with an apparatus-absorber effective area of 0.2 $m^2$. Outdoor experiments were carried out to demonstrate the applicability of using a compact solar collector for water heating. The time-wise temperatures of the PCM were recorded during the processes of charging and discharging. The solar intensity was recorded during the charging process. Experiments were conducted for different water flow rates of 8.3–21.7 kg/h. The effect of the water flow rate on the useful heat gain was studied. The heat transfer coefficients were calculated for the charging process. The propagation of the melting and freezing front was also studied during the charging and discharging processes. The experimental results showed that in the charging process, the average heat transfer coefficient increases sharply with increasing the molten layer thickness, as the natural convection grows strong. In the discharge process, the useful heat gain was found to increase as the water mass flow rate increases (Fig. 7).

Cabeza et al. [36] constructed solar pilot plant at the University of Lleida to test the PCM behavior in real conditions, which could work continuously with the solar system, or could also work with an electrical heater. The PCM module geometry adopted was to use several cylinders at the top of the water tank. Several experiments with two, four and six PCM modules were carried out in the real installation. A granular PCM–graphite compound of about 90 vol.% of sodium acetate trihydrate and 10 vol.% graphite was chosen as the PCM for the experiments presented here. Author concluded that the inclusion of a PCM module in water tanks for domestic hot-water supply is a very promising technology. It would allow to have hot water for longer periods of time even without exterior energy supply, or to use smaller tanks for the same purpose.

Suat et al. [37] presented a conventional open-loop passive solar water-heating system combined with sodium thiosulfate pentahydrate-phase change material (PCM) were experimentally investigated during November and then enhancement of solar thermal energy storage performance of the system by comparing with those of conventional system including no PCM was observed. Heat storage performances of the same solar water-heating system combined with the other salt hydrates-PCMs such as zinc nitrate hexahydrate, disodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate and sodium sulfate decahydrate (Glauber's salt) were examined theoretically by using meteorological data and thermophysical properties of PCMs with some assumptions. It was obtained that the storage time of hot water, the produced hot water mass and total heat accumulated in the solar water-heating system having the heat storage tank combined with PCM were approximately 2.59–3.45 times of that in the conventional solar water-heating system. It was also found that the hydrated salts of the highest solar thermal energy storage performance in PCMs used in theoretical investigation were disodium hydrogen phosphate dodecahydrate and sodium sulfate decahydrate (Fig. 8).

### 5.2. Solar air heating systems

Morrison, Abdel Khalik and Jurinak in their different studies [38,39] evaluated the performance of air-based solar heating systems utilizing phase change energy storage unit. The main objectives of their work were: (i) to determine the effect of the PCM latent heat and melting temperature on the thermal performance of air-based solar heating systems and (ii) to

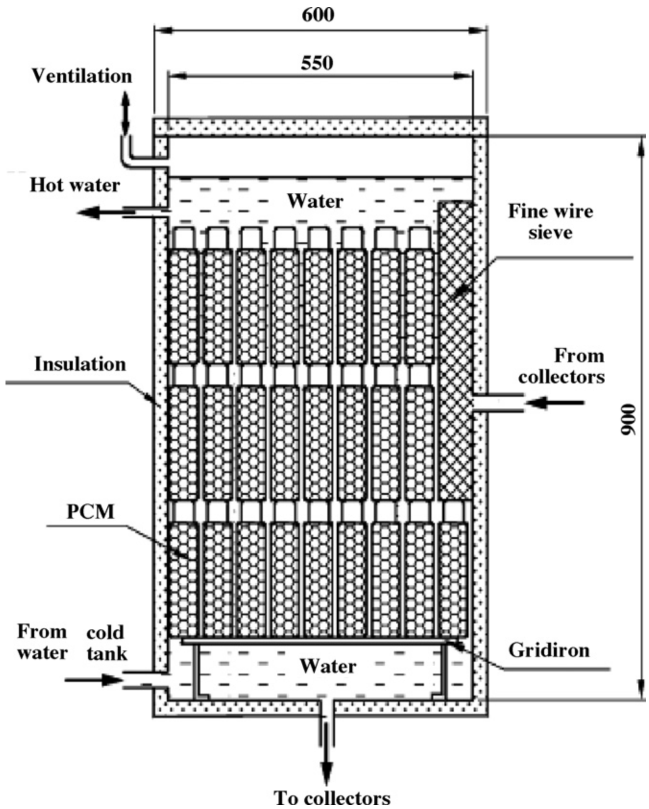



Fig. 8. Detailed cross-sectional view of the cylindrical heat storage tank combined with PCM.

develop empirical model of significant phase change energy storage (PCES) units. The main conclusion was that the PCM should be selected on the basis of melting point rather than its latent heat and also found that air-based system utilizing sodium sulfate decahydrate as a storage medium requires roughly one-fourth the storage volume of a pebble bed and one-half the storage volume of a water tank. Ghoneim and Klein [40] compared theoretically the performance of phase change and sensible heat storage for air and water based solar heating systems. Sodium sulphate decahydrate and paraffins were used as phase change materials and noted the similar results as by Jurnik and Adbel Khalik [39].

Enibe [41] designed, development and performance evaluation of a natural convection solar air heater with phase change material energy storage has been successfully undertaken. The daytime performance of the system under no-load conditions was tested under natural environmental conditions involving ambient temperature variations in the range 19–41 °C and daily global irradiation in the range 4.9–19.9 MJ $m^{-2}$. Peak temperature rise of the heated air was about 15 K, while peak cumulative useful efficiency was about 50%. The system is suitable for use as a solar cabinet crop dryer for aromatic herbs, medicinal plants and other crops, which do not require direct exposure to sunlight (Fig. 9).

Zhou et al. [42] investigated numerically the performance of a hybrid heating-system combined with thermal storage by shape-stabilized phase-change material (SSPCM) plates. A direct gain passive-solar house in Beijing is considered: it includes SSPCM plates as inner linings of walls and the ceiling. Unsteady simulation is performed using a verified enthalpy model, with a time period covering the winter heating-season. Additional heat supply is employed during load hours at late night and early morning or during the whole day necessary to keep the minimum indoor air temperature above 18 °C. The results indicate the thermal-storage effect of SSPCM plates, which improves the indoor thermal comfort level and saves about 47% of normal-and-peak-hour energy use and 12% of total energy consumption in winter. This hybrid heating system can level the electrical load for power plants and would provide significant economic benefits in areas where night and day electricity tariff policy is used.

### 5.3. Solar cookers

One of the major uses of solar energy is in cooking using different types of solar cookers. Use of these solar cookers is




Fig. 9. Photograph of the air heating system. (A) Collector assembly with energy storage and air-heating subsystems; (B) heated space.

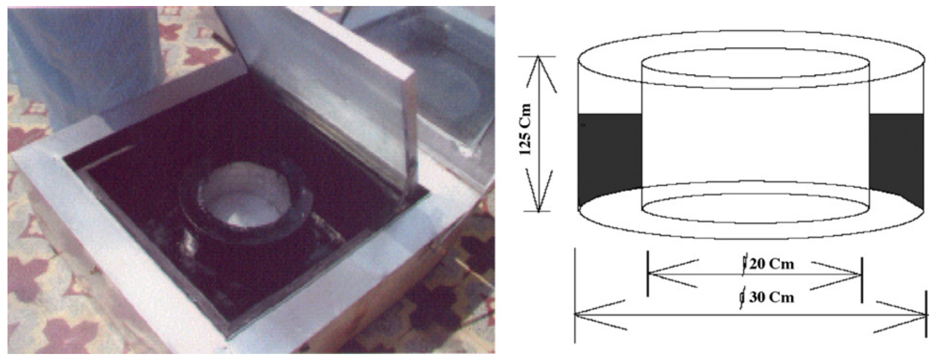



Fig. 10. Schematic diagram of the box of a solar cooker with storage.

limited, as cooking of food is not possible in the evening. If storage of solar energy is provided in a solar cooker, than the utility and reliability of these solar cookers would increase. Few studies have been conducted with the latent heat storage materials in a box type solar cooker to cook the food in the late evening. Domanski et al. [43] have studied the use of a PCM as a storage medium for a box type solar cooker designed to cook the food in the late evening hours and/or during the non-sunshine hours. They used magnesium nitrate hexahydrate ($Mg(NO_3)_2\cdot 6H_2O$) as a PCM for the heat storage. Buddhi and Sahoo [44] filled commercial grade stearic acid below the absorbing plate of the box type solar cooker. Sharma et al. [45] developed a PCM storage unit with acetamide for a box type solar cooker to cook the food in the late evening (Fig. 10). They recommended that the melting temperature of a PCM should be between 105 and 110 °C for evening cooking. Later Buddhi et al. [46] developed a storage unit with acetanilide for a box type solar cooker to store a larger quantity of heat through a PCM, so that they used three reflectors to get more input solar radiation. But generally in a box type solar cooker only one reflector is used. Sharma et al. [47] also used erythritol as a latent heat storage material for the solar cooker based on an evacuated tube solar collector (Fig. 11).

### 5.4. Solar green house

Phase change materials have also been used in green houses for storing the solar energy for curing and drying process and plant production [48]. Kern and Aldrich [49] employed 1650 kg of $CaC1_2\cdot 6H_2O$ in aerosol cans each weighing 0.74 kg was used to investigate energy storage possibilities both inside and outside a 36 $m^2$-ground area greenhouse covered with tedlar-

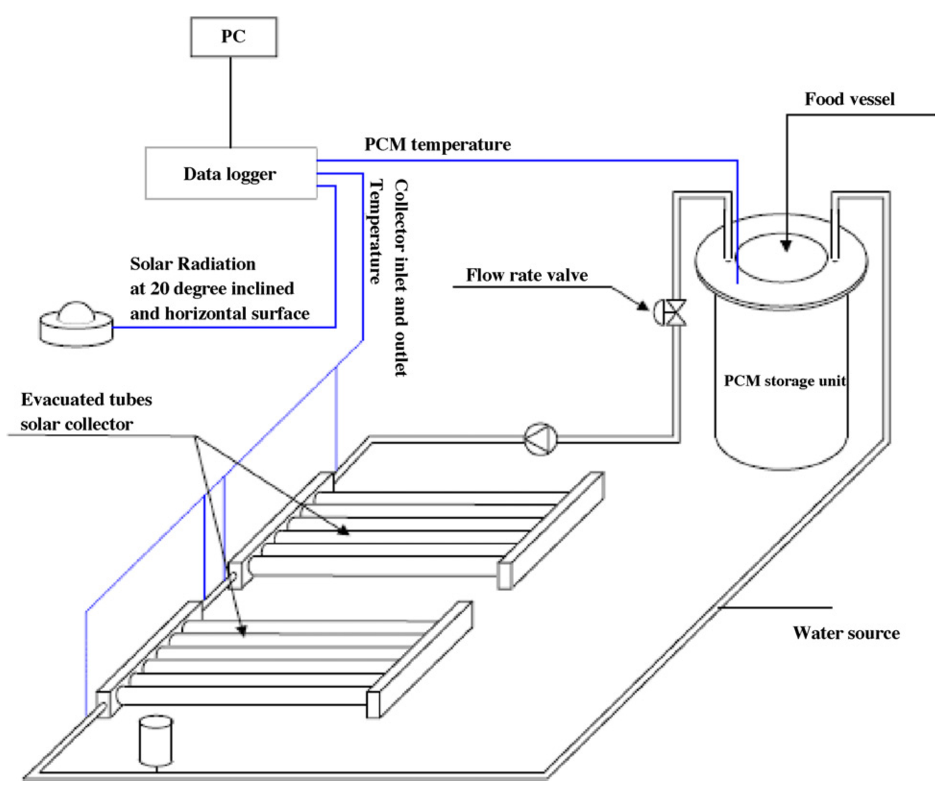



Fig. 11. Outline of the prototype solar cooker based on evacuated tube solar collector with PCM storage unit.

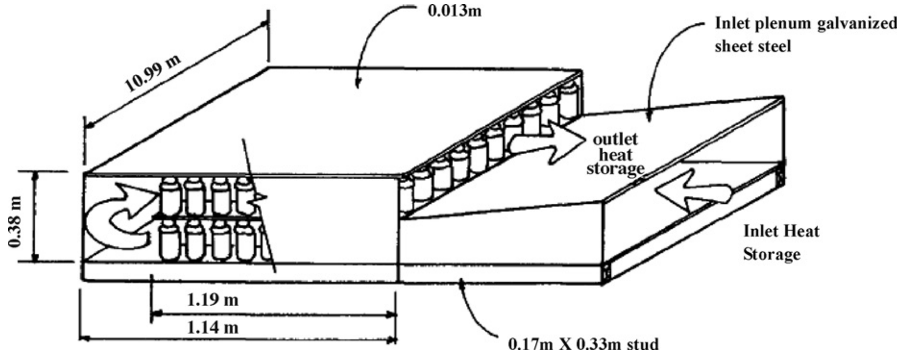


Fig. 12. Energy storage unit inside the greenhouse.

coated fibreglass. PCM cans were placed in a store with 22.86 mm spacing and two stores containing different amounts of PCM was used, one inside and the other outside the greenhouse. While the energy storage unit inside the greenhouse collected warm air from the ridge of the greenhouse during the daytime, the direction of air flow was reversed for the energy releasing process at night (Fig. 12).

Hung and Toksoy [50] had designed and constructed a latent heat storage system with two different stacking configurations and air baffling as an integrated part of the greenhouse solar system. Commercial cylindrical storage rods were used as the primary storage elements. The results showed that the designed latent storage systems demonstrated significantly higher compact storage capacity than the rock or water storage. It is also revealed that the ring-baffled storage unit performed better than the cross-baffled storage unit. Using phase change material, experiments were conducted in a 500 $m^2$ single glazed greenhouse for the production of rose in France (Fig. 13). The solar heat available inside the greenhouse was transferred and stored by recycling the air through an underground of flat heat exchangers filled with a PCM. The performance of solar greenhouse compartment with PCM storage was compared with a traditional greenhouse of identical geometry having the same plantation. The PCM green house achieved 80% savings in propane gas as compared with the traditional green house to have the same temperature. Latent heat storage material can also be stacked in racks placed in a greenhouse which will be directly heated by the solar radiation [51]. In this system the hot air was circulated in the greenhouse through the storage to increase the rate of charging/discharging of PCM. The stored heat was utilized during off sunshine hours to maintain the desired temperature of the green house. $Na_2SO_4{\cdot}10H_2O$ was used as PCM storage material in the green house.

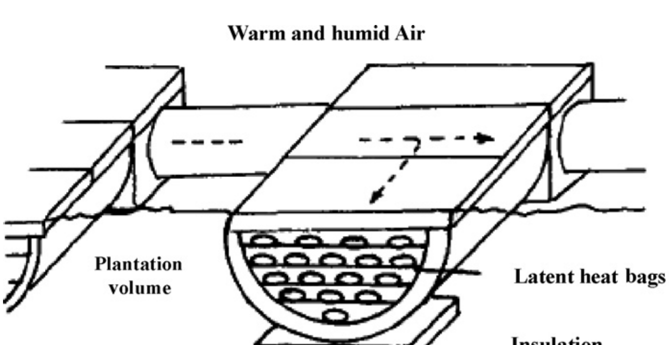


Fig. 13. Underground tunnel with PCM Storage.

Nishina and Takakura [52] used $Na_2SO_4{\cdot}10H_2O$ with some additives to prevent phase separation and degradation for heating a greenhouse in Japan. Fig. 14 shows the general view of the experimental set-up. They concluded that 40–60% of the latent heat potential of the PCM was realized, which indicated that almost half of the PCM was not used efficiently during the energy exchange processes. Takakura and Nishina [53] tested polyethylene glycol and $CaCl_2{\cdot}6H_2O$ as PCMs in greenhouse heating for 7.2 $m^2$ ground area. They compared conventional greenhouses with PCM storage type greenhouses. The efficiency of the greenhouse with PCM storage integrated with solar collector was 59% and able to maintain 8 °C inside the greenhouse at night, when the outside temperature dropped to −0.6 °C. A microcomputer control system has been developed in order to establish more accurate and more sophisticated control for solar greenhouse systems.

In a design and experimentation study by Baille and Boulard [54] and Boulard et al. [55] $CaC1_2{\cdot}6H_2O$ melting at 21 °C was utilized in a greenhouse with 176 $m^2$ ground area, double polycarbonate-cover and forced ventilation (Fig. 15). Thermostat settings for night and day in February and March were, respectively, 12 and 14, and 22 and 26 °C. Air velocity in the greenhouse had an order of magnitude 1 m/s. It was calculated that while 0.260 kW h/$m^2$ energy was stored during the daytime, 0.360 kW h/$m^2$ was released at night in the greenhouse. When the outside air temperatures were 3.8 and 6.6 °C, respectively, in February and March, inside air temperatures for the same periods of 10.9 and 13.5 °C were obtained. With this

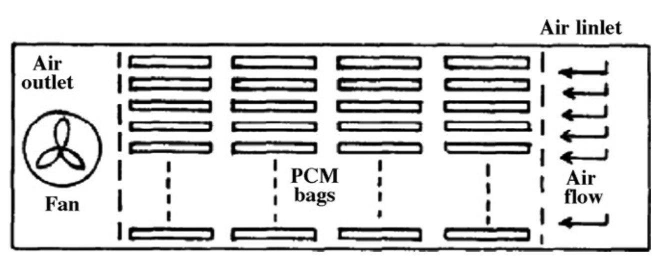


Fig. 14. General view of the phase change energy storage system in green house.

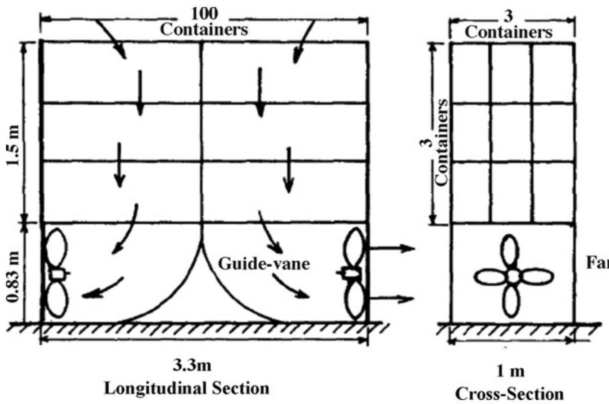


Fig. 15. General view and dimensions of the energy storage unit.

method, instead of what would be 7.2 $1/m^2$ fuel requirement, 40% of heating load was supplied and an overall 30% in energy saving was achieved.

Ozturk [56] presented a seasonal thermal energy storage using paraffin wax as a PCM with the latent heat storage technique was attempted to heat the greenhouse of 180 $m^2$ floor area. The schematic arrangement of the LHS system for greenhouse heating is given in Fig. 16. The system consists mainly of five units: (1) flat plate solar air collectors (as heat collection unit), (2) latent heat storage (LHS) unit, (3) experimental greenhouse, (4) heat transfer unit and (5) data acquisition unit. The external heat collection unit consisted of 27 $m^2$ of south facing solar air heaters mounted at a 55° tilt angle. The diameter and the total volume of the steel tank used as the latent heat storage unit were 1.7 m and 11.6 $m^3$, respectively. The LHS unit was filled with 6000 kg of paraffin, equivalent to 33.33 kg of PCM per square meter of the greenhouse ground surface area. Energy and exergy analyses were applied in order to evaluate the system efficiency. The rate of heat transferred in the LHS unit ranged from 1.22 to 2.63 kW, whereas the rate of heat stored in the LHS unit was in the range of 0.65–2.1 kW. The average daily rate of thermal exergy transferred and stored in the LHS unit were 111.2 W and 79.9 W, respectively. During the experimental period, it was found that the average net energy and exergy efficiencies were 40.4% and 4.2%, respectively. The effect of the temperature difference of the heat transfer fluid at the inlet and outlet of the LHS unit on the computed values of the energy and exergy efficiency is evaluated during the charging period.

### 5.5. Buildings

PCMs have been considered for thermal storage in buildings since before 1980. With the advent of PCM implemented in Trombe wall, wallboards, shutters, under-floor heating systems and ceiling boards can be use as a part of the building for heating and cooling applications. In the literature, development and testing were conducted for prototypes of PCM wallboard and PCM concrete systems to enhance the thermal energy storage (TES) capacity of standard gypsum wallboard and concrete blocks, with particular interest in peak load shifting and solar energy utilization.

The application of PCMs in building can have two different goals. First, using natural heat that is solar energy for heating or night cold for cooling. Second, using manmade heat or cold sources. In any case, storage of heat or cold is necessary to match availability and demand with respect to time and also with respect to power. Basically three different ways to use PCMs for heating and cooling of buildings are:

(i) PCMs in building walls,
(ii) PCMs in other building components other than walls, and
(iii) PCMs in heat and cold storage units.

Different applications for latent heat thermal energy storage (LHTES) in buildings are given below.

#### 5.5.1. PCM Trombe wall

Several authors have proposed the inclusion of phase change materials in walls partitions ceilings and floors to serve as temperature regulators. The phase change materials have been

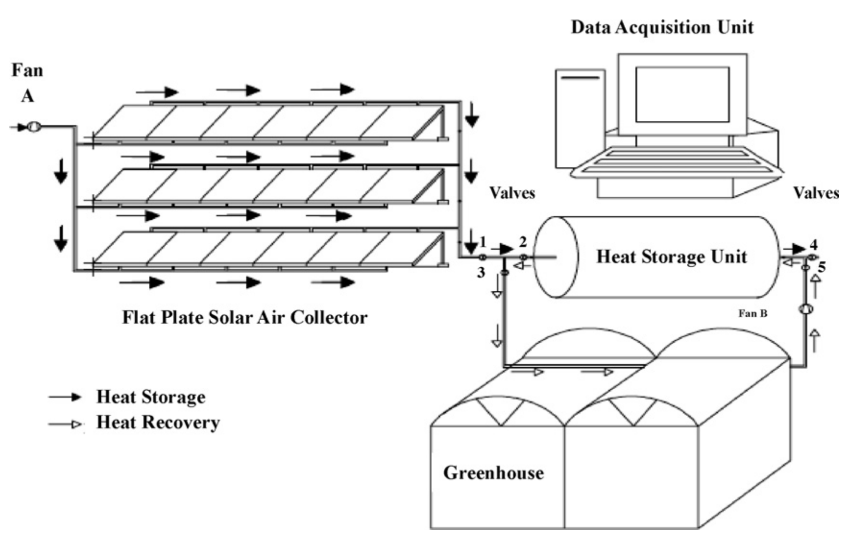


Fig. 16. The arrangement of the heat storage and greenhouse heating system.

used to replace masonry in a Trombe wall. Experimental and theoretical tests have been conducted to investigate the reliability of PCMs as a Trombe wall [57,58]. For a given amount of heat storage, the phase change units require less space than water walls or mass Trombe walls and are much lighter in weight. These are, therefore, much convenient to make use of in retrofit applications of buildings. Commonly used PCMs are salt hydrates and hydrocarbons. Metallic additives was used for increasing the overall conductivity and efficiency.

In order to provide a better picture of how PCM latent heat storage can help to improve thermal performance of an ordinary Trombe wall for passive solar heating. The analysis evaluated transient temperature of an ordinary concrete Trombe wall having thicknesses of 30 cm (12 in.) and 10 cm (4 in.). The resulting data were compared with those of the same wall design configuration but having 20% by weight of a paraffin-type PCM homogeneously mixed with the concrete wall material. Castellon et al. [59] studied a Trombe wall was recently added to the south façade to investigate if the effect of the PCM can be used all year long in Mediterranean weathers to reduce both cooling and heating demands. The configuration of the Trombe wall model is illustrated in Fig. 17.

Bourdeau [60] tested two passive storage collector walls using calcium chloride hexahydrate (melting point 29 °C) as a phase change material. He concluded that an 8.1 cm PCM wall has slightly better thermal performance than a 40-cm thick masonry wall. Experimental and theoretical tests were conducted to investigate the reliability of PCMs as a Trombe wall [61–63] used sodium sulfate decahydrate (melting point 32 °C) as a phase change material in south facing Trombe wall. They also reported that Trombe wall with PCM of smaller thickness was more desirable in comparison to an ordinary masonry wall for providing efficient thermal energy storage. Knowler [64] used commercial grade paraffin wax with metallic additives for increasing the overall conductivity and efficiency in the Trombe wall. Stritih and Novak [65] presented a solar wall for building ventilation, which absorb solar energy into black paraffin wax (melting point, 25–30 °C). The stored heat was used for heating the air for the ventilation of the house. The efficiency of the absorption was found to be 79%. The result of the simulation showed that the panel dictates the amount of stored heat as sensible or latent and that the melting point of the PCM has an influence on the output air temperature. The analysis for the heating season gave the optimum thickness of 50 mm and the melting point a few degrees above the room temperature.

### 5.5.2. PCM wallboards

The wallboards are cheap and widely used in a variety of applications, making them very suitable for PCM encapsulation. However, the principles of latent heat storage can be applied to any appropriate building materials. Processes where by this PCM could be incorporated into plasterboard either by post manufacturing imbibing of liquid PCM into the pore space of the plasterboard or by addition in the wet stage of plasterboard manufacture were successfully demonstrated. The idea of improving the thermal comfort of lightweight buildings by integrating PCMs into the building structure has been investigated in various research projects over several decades given by Kedl and Stovall [66] and Salyer and Sircar [67], Shapiro et al. [68], Shapiro [69], Feldman et al. [70–72], Hawes et al. [73], Neeper [74–76], Stovall and Tomlinson [77], Drake [78], Peippo et al. [79], Feustel and co-workers [80], Athienitis et al. [81], Kissock et al. [82], Kalousek and Hirs [83]. Most of these attempts applied macro-capsules or direct immersion processes, which both turned out to present several drawbacks. Due to these problems, none of these PCM products was successful in the wider market. The new option to micro-encapsulate PCMs, a key technology which overcomes many of these problems, may make PCM products accessible for the building industry. Schossig et al. [84] described the work done at Fraunhofer ISE within a German government-funded project over the last 5 years, extending from building simulations to first measurements of full-size rooms equipped with PCM. The first products are now available on the market (Fig. 18).

### 5.5.3. PCM shutter

In this concept, shutter-containing PCM is placed outside of window areas. During daytime they are opened to the outside the exterior side is exposed to solar radiation, heat is absorbed

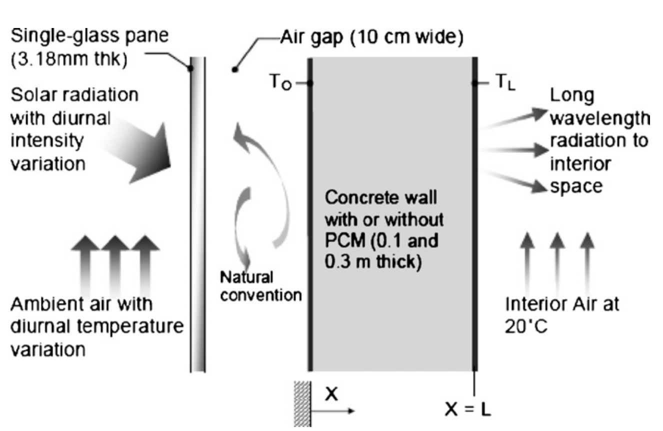



Fig. 17. Configuration of the tested Trombe wall model.

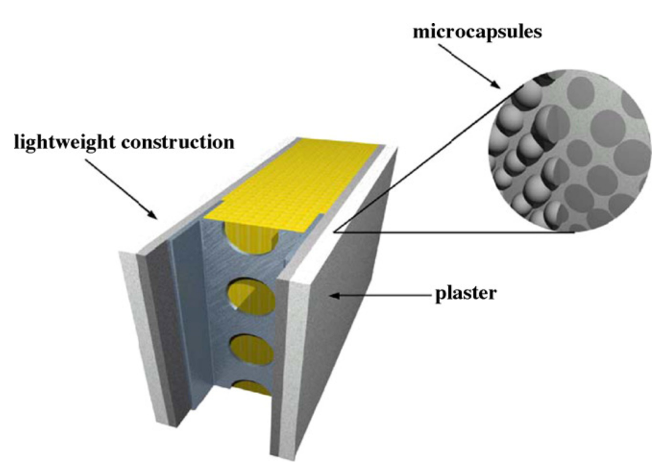



Fig. 18. Schematic view of a lightweight wall. The PCM micro-capsules are integrated into the interior plaster.

and PCM melts. At night we close the shutter, slide the windows and heat from the PCM radiates into the rooms. Harald Mehling [85] presented his project report at 8th Expert Meeting and Work Shop, Kizkalesi, Turkey on the ''Innovative PCM-Technologies'' and suggested to use the PCM shutters with windows. He recommended through the use of the PCM shutters the maximum shading temperature delayed by 3 h, room temperature reduced by 2° (Fig. 19).

### *5.5.4. Under-floor heating systems*

Floor is also the important part of a building and heating and cooling of buildings were tried using it. Athienities and Chen [86] investigated the transient heat transfer in floor heating systems. His study focused on the influence of the cover layer and incident solar radiation on floor temperature distribution and on energy consumption. Complete and partial (area) carpets were considered as well as hardwood cover layers over concrete or gypcrete (gypsum–concrete mixture) thermal storage. Experimental and simulation results for an outdoor test room reveal that solar beam radiation can cause a local floor surface temperature in the illuminated area 8 °C higher than that in the shaded area. Partial carpet cover further increases floor surface temperature difference up to 15 °C when solar radiation was absorbed. Solar radiation stored in the floor thermal mass was found to reduce heating energy consumption significantly (30% or more). Increase of thermal mass thickness from 5 cm to 10 cm did not lead to higher energy savings with conventional proportional-integral control. Advanced control algorithms need to be developed to maximize energy saving while maintaining good thermal comfort.

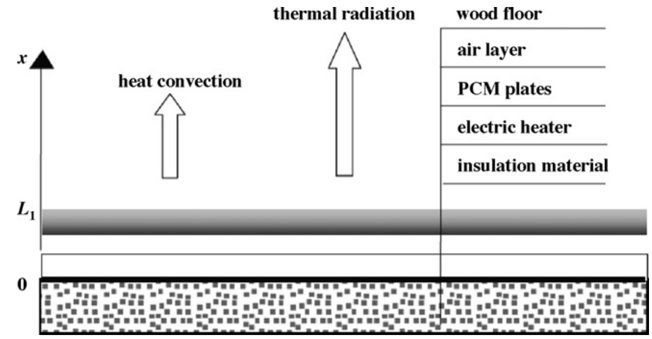



Fig. 20. Schematic of under-floor electric heating system with shape stabilized PCM plates.

Radiant heating has a number of advantages over convective air heating systems. It saves living and working space since it is integrated into the building envelope. Also, thermal mass integrated into a floor heating system can be used for off-peak storage of thermal energy. Thus, peak loads may be reduced and shifted to nighttime when electricity costs are lower [87]. From an application point of view, dense materials such as concrete may cause larger fluctuations of indoor temperature, while PCMs can provide large latent heat storage over the narrow range of temperatures typically encountered in buildings, thus they can improve the thermal comfort level. Fig. 20 shows the schematic of an under-floor electric heating system with shape-stabilized PCM plates which include polystyrene insulation, electric heaters, PCM, air layer and wood floor [88]. Electric heaters heat and melt the PCM layer by using cheaper nighttime electricity and the system stores heat. During the day the




Fig. 19. PCM shading.

electric heaters are switched off and the PCM layer solidifies, discharging the heat stored. In many cities in China, the electricity tariff at night is 1/3–1/5 of that during the day. Therefore, the shift of electrical consumption from peak periods to off-peak periods will provide significant economic benefit. Moreover, it is of importance to power plants by leveling the electrical load.

Nagano et al. [89] presented a floor air conditioning system with latent heat storage in buildings. Floor size of the experimental cell was 0.5 $m^2$. Granulated phase change material was made of foamed waste glass beads and mixture of paraffin. The PCM packed bed of 3 cm thickness was installed under the floorboard with multiple small holes. The change in room temperature and the amount of stored heat were measured and results showed the possibilities of cooling load shifting by using packed granulated PCM.

*5.5.5. Ceiling boards*

Ceiling boards are the important part of the roof, which are utilized for the heating and cooling in buildings. Bruno [90] developed a system, which stored coolness in phase change material in off-peak time and released this energy in peak time. The effects of the peak-cut control of air-conditioning systems using PCM for ceiling board in the building were also tried. The melting point of the PCM used was of the range 20–30 °C, which was almost equal to the room temperature suitable for the purpose. Latent heat solar roof was tested in a Peruvian village to maintain near isothermal conditions in an experimental chicken brood. The brooder house was divided into two connecting parts, a patio and a heated enclosure. Two semi-circular tanks with upper face closed with glass, containing 42 kg of paraffin wax each were located below a glass roof, which was airtight. At night thick polyurethane insulators were placed between the glass roof and paraffin tanks to regulate the enclosure temperature between 22 and 30 °C given by Benard et al. [91].

A space heating system that incorporates a PCM located in the ceiling void was developed by Gutherz and Schiler [92]. Sun reflectors were used to direct the solar energy entering via the windows on to the PCMs. The main advantage of the system was that it allowed a large area to be dedicated to heat storage without the need for large volumes of storage medium that would be required with sensible heat storage. It was shown that the use of such a system has the potential to recover 17–36% of heat lost over the initial gains. Turnpenny et al. [93] developed a latent heat storage unit incorporating heat pipes embedded in phase change material. A one-dimensional mathematical model of the heat transfer from air to PCM was presented to allow sizing of a test unit. His system stored coolness in nighttime and released the store coolness in daytime.

Kodo and lbamoto [94] examined the effects of a peak shaving control of air conditioning systems using PCM (phase change material) for ceiling boards in an office building. Rock wool PCM ceiling board (PCM ceiling board) was enhanced by adding micro-capsulate PCM, with a melting point, of about 25 °C, close to room temperature. In this system, a PCM ceiling board is used instead of a rock wool ceiling board. Fig. 21 shows an outline of the system. During overnight thermal storage, the cool air from the AHU flows into the ceiling chamber space and chills the PCM ceiling board, thus storing cooling thermal energy. The cooling thermal energy was stored using cut-rate electricity (Fig. 21a). During normal cooling time, the cool air from the AHU flows directly into the room (Fig. 21b). During peak shaving time, when the thermal load peaks, the air from the room returns to the AHU via the ceiling chamber space. As a result of passing through the cooled-down PCM ceiling board, the warm air returning from the room is pre-cooled on its way back to the AHU (Fig. 21c). The maximum thermal load and the capacity of the heat source can thus be reduced. Normal cooling time is from 7 a.m. to 1 p.m. The peak shaving time is from 1 p.m. to the end of business hours. In this study, the thermal-storage time is from 4 a.m. to

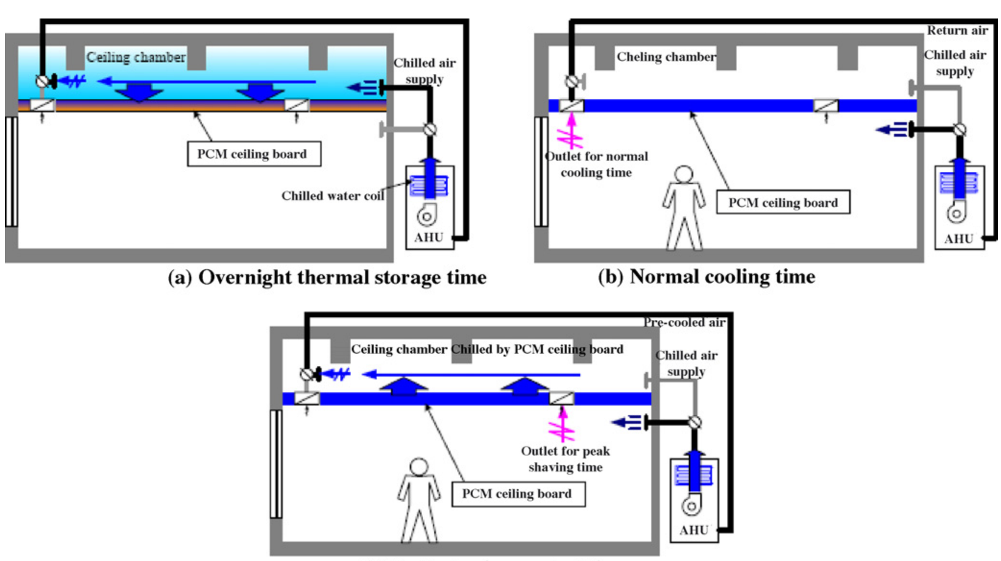



Fig. 21. Outline of the ceiling board system.

7 a.m. The reduced use of maximum-charge electricity during the peak shaving period and the use of cheaper-rate nighttime electricity result in lower energy costs.

This thermal-storage system has the following advantages over conventional building thermal-storage systems that use concrete floor slabs.

(1) More efficient thermal storage is expected, since high-density cool air pools on the PCM ceiling board that forms the floor of the ceiling space.
(2) All of the ceiling board can be used for thermal storage, since the cool air can flow through the ceiling chamber without being interrupted by beams.
(3) Since the surface temperature of the ceiling board is kept at the PCM melting point for an extended period, the indoor thermal environment, including the radiant field, can be improved.

### 5.6. Off-peak electricity storage

Telkes [95], Herrick [96] and Gawarn and Scroder [97] studied latent heat storage system for air conditioning. Inorganic hydrous salts were used as storage material. However these studies were focused more on the development of new heat storage materials. Lane [98] suggested some PCMs for cooling and dehumidification. The PCM is frozen during off-peak hours and coolness is withdrawn as needed during the day. Recently Department of Atomic Energy, Govt. of India sanctioned a R&D project to develop latent heat storage materials for the temperature range 5–15° for the storage of the coolness using off-peak power and to develop the pilot plant for the same [99] (Fig. 22).

Several efforts have been made to develop PCM storage systems to utilize off-peak electricity [100–103]. Using off-peak electricity, phase change material can be melted/frizzed to store electrical energy in the form of latent heat thermal energy and the heat/coolness then is available when needed. So, if latent heat thermal energy storage (LHTES) systems are coupled with the active systems, it will help in reducing the peak load and thus electricity generation cost can be reduced by keeping the demand nearly constant. Brandstetter and Kaneff [104] studied the low cost salt-hydrate phase change materials (PCMs) as candidate media for thermal storage and modified varieties covering a range of transition temperatures about 8–58 °C. Authors also concluded that these salt hydrates could be used for off-peak space heating and solar greenhouse climate control. Farid and Hussain [105] and Theunissen and Buchlin [106] developed an electrical storage heater utilizing off-peak electricity, usually available at night and the performance was tested experimentally and theoretically. Heat was stored in a commercial grade paraffin wax as latent heat of fusion to reduce the heavy weight of the existing storage heaters having sensible heat of storage. PCM was filled in multi units arranged to supply the necessary heat to the air flowing through them.

Mostly active floor system can be used for off-peak storage of thermal energy in buildings. Thus, peak loads may be reduced and shifted to nighttime when electricity costs are lower. An electrical under-floor heating system having paraffin wax (melting point, 40 °C) as the PCM was proposed by Farid and Chen [107]. They placed 30-mm layer of PCM between the heating surface and the floor tiles. Using computer simulation they found that the heat output of the floor could be raised significantly from 30 W/m$^2$ to 75 W/m$^2$ if PCM storage was used.

### 5.7. Design of heat exchanger for thermal energy storage

Generally the phase change material have low thermal conductivity and expand on melting therefore, the design of a suitable heat exchanger is an important component of a latent heat storage system. Various kind of heat exchanger were tried by a number of researchers and are a given under. Buddhi [108] designed and fabricated a PCM based shell and tube type heat exchanger without fins for low temperature industrial waste heat recovery. To improve the effective thermal conductivity of the system, the radial distance among the tubes was kept 3–4 cm. He studied the thermal performance of this heat exchanger for charging and discharging process of PCM for different mass flow rates and temperature of the inlet water. Commercial grade stearic acid has been used as a phase change material and filled up to about 90% of the volume. Due to poor thermal conductivity of PCM, the value of overall heat transfer

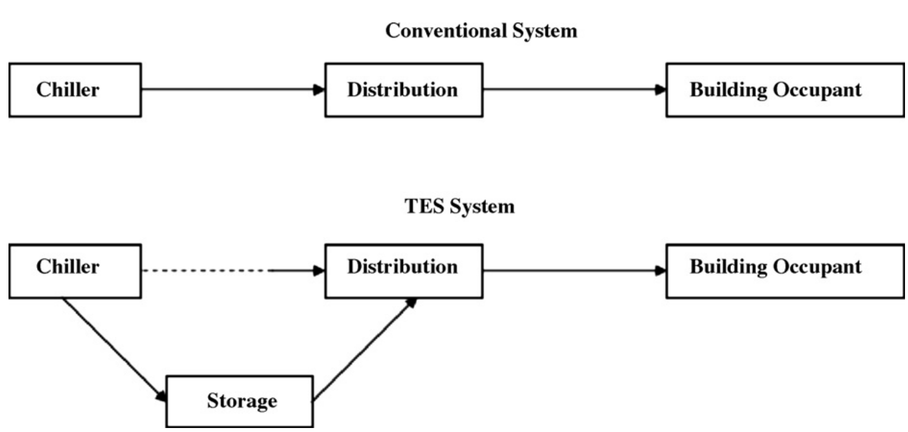



Fig. 22. Major system cooling components.

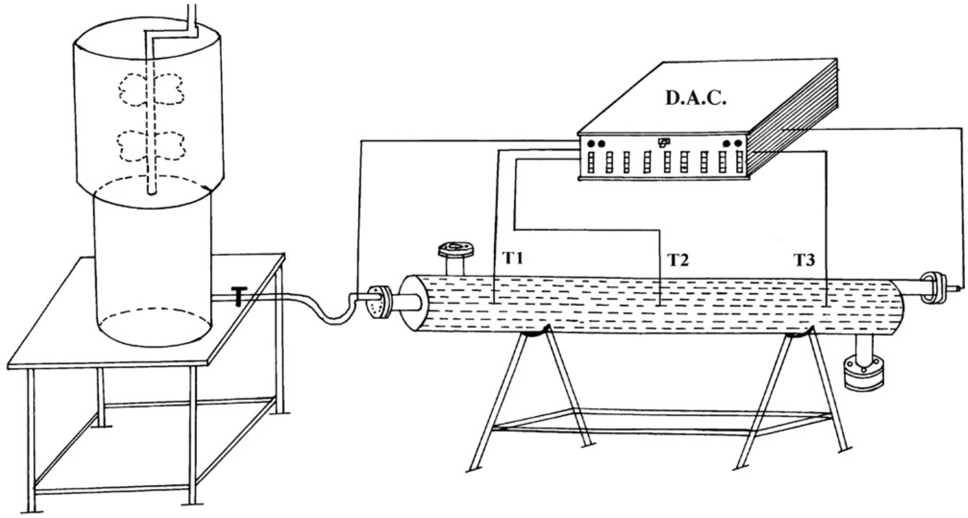



Fig. 23. Schematic diagram of a shell and finned tube type heat exchanger with heat storage and two stages feed water tank.

coefficients was founded low. Schematic diagram of a shell and finned tube type heat exchanger with heat storage and two stage feed water tank are shown in Fig. 23. Finned heat pipe heat exchanger [109], which consists of a container of a square cross-section, provided with heat pipe along its longitudinal axis. The outer surface of the tube, which comes in contact with PCM, was chromed due to considerations of material compatibility. The container as well as the heat pipe are divided into three regions, heat sources region, storage region and heat sink region, respectively. The heat pipe in the storage region was provided with closely and equally spaced circular aluminum fins. Calmac Corporation [110] developed an active storage system for solar space heating and solar space cooling. It employed close-spaced (small diameter) plastic tubing mat coiled into a spiral and inserted into a cylindrical tank containing PCM, as a heat exchanger. The system employed salt hydrate (PCM) consisting of 98% sodium thiosulphate pentahydrate and 2% sodium sulfate for space heating applications and magnesium chloride hexahydrate for space cooling units. The plastic heat exchanger had the advantage of low cost and being non-corrosive. 1.27 cm diameter plastic tubing with 2.5 cm spacing takes care of poor thermal conductivity of PCM. The system was successfully tested for 1000 cycles without any degradation in the performance of the system. Smith et al. [111] studied a heat exchange consists of a rectangular container for the PCM with a rectangular flow channel underneath it. Gulf wax 33 (m.p. 50–55 °C) was used as a latent heat storage material. He found that the system had a limitation of the heat transfer due to resistance of the solid phase. The additional heat path provided by the conducting container wall that reduced this resistance significantly. Morcos [112] studied an experimental investigation of a shell-and-tube heat exchanger concept for the use in a latent heat thermal energy storage system for solar heating applications. The thermal analysis provided the influence of the water inlet temperature and mass flow rate on the storage charging, discharging times and temperature gradient for heat flow into or out of two different storage substance: paraffin wax and asphalt. Asphalt is used for the first time as an energy storage material, to test the storage capacity. Cho et al. [113] studied the heat transfer characteristics during melting of magnesium chloride hexahydrate in circular finned and unfinned tube system. Herrick [114] studied the detailed description of the rolling cylinder for solar cooling and heating and after that use the PCM: glauber's salt in the rolling heat exchanger. Santamouris and Leafs [115] designed and developed a rolling cylinder heat exchanger design and investigated the problem arising in the coupling of the storage to the thermal system. The designed rolling cylinder heat exchanger consisted of a collection of smaller sub-units each of cylinder shape, in which actual energy storage took place. The storage system consisted of a number of heat exchanger modules operated in parallel. Each module consisted of a number of cylinders mounted on a larger one so that they can be rotated as a single unit. The objective of the rotation was to provide complete freezing. Bouritios et al. [116] also studied the problems arise in the architecture of heat exchanger and coupling to the active system and the load. Farid and Kanzawa [117] studied the performance of a heat storage unit consisting of cylindrical capsules filled with phase change materials, with air flowing across them for heat exchange. They used the three commercial waxes with melting temperatures 44, 53, and 64 °C. Rectangular arrangements for the tubes were used with longitudinal and transverse. A considerable improvement in the performance of the storage unit was achieved by using more than one type of PCM, with a narrow melting range in the same unit and encapsulation.

## 6. Heat transfer in latent heat thermal energy storage systems and materials

The study of heat transfer characteristics of melting and solidification process is also one of the most attractive areas in contemporary heat transfer research.

### 6.1. The Stefan problem

In 1989 Stefan [118] in his work on the freezing of the ground posed and solved the following problem:

The heat conducting material occupies the space—$\infty < x < \infty$. At the initial time the liquid phase fills the domain $0 < x < \infty$ at temperature $T_1 > 0\,^\circ\mathrm{C}$ while the solid occupies the domain—$\infty < x < 0$ at temperature $T_S < 0\,^\circ\mathrm{C}$. At $x = 0$, it is maintained at constant temperature $T < 0\,^\circ\mathrm{C}$, under the effect of which the solidification occurs isothermally at temperature $T_m = 0\,^\circ\mathrm{C}$ without supercooling and conduction is the mode of heat transfer in the material. The energy equation at the solid–liquid interface given by Stefan is

$$\lambda\rho\left(\frac{\mathrm{d}s(t)}{\mathrm{d}t}\right) = k_s\left(\frac{\delta T_s}{\delta t}\right) - k_l\left(\frac{\delta T_l}{\delta t}\right) \tag{8}$$

Eq. (8) arises in the presence of phase change and expressing the energy conservation across the interface. In literature, this solid–liquid interface boundary is known as Stefan or moving boundary problem.

### 6.2. Different techniques for solving the Stefan problem

The problem of predicting the behavior of phase change systems is difficult due to its non-linear nature at moving interface and in addition, the two phases have different thermophysical properties. Classically, the Stefan problem was first approached as a pure conduction in semi-infinite medium [119,120] and later on natural convection has been considered during melting and solidification of phase change materials. The different classes of solution available for Stefan problem are analytical and numerical. Many approximate analytical techniques such as the heat balance integral [121,122], variation technique [123], isothermal migration [124], source and sink method [125] and periodic solution [126]. A common drawback of these approximate techniques is limited to one-dimensional analysis and they become very complicated when applied to multidimensional problem. Numerical methods, both finite difference [127,128] and finite element [129,130] appear more powerful in solving the moving boundary problem. In general, a time variant mesh approach [131,132] offers good accuracy but is limited to simple problems and geometry's. The fixed mesh approach [133–135], in which the latent heat of fusion is usually absorbed into the material's specific heat or enthalpy, is much simpler in practical application.

A common problem in latent heat thermal storages is the poor conductivity of the PCMs. During the phase change the solid–liquid interface moves away from the heat transfer surface. One of the way to increase the effective heat transfer area is that the PCM container side walls of high thermal conducting material be closely spaced. The difficulty in solving a phase change problem is the presence of a moving boundary or region on which heat and mass balance conditions have to be met. Generally, two approaches of the finite difference and finite element techniques are used to solve the phase change problems numerically. One of the methods to solve the moving boundary problem is enthalpy formulation [136–139]. The enthalpy method is used in a particular way so that the only unknown variable is the temperature of the phase change material and the solidification occurs at a uniform temperature. Enthalpy method treats the enthalpy as a temperature dependent variable and constructs the latent heat flow through the volume integration with the use of the enthalpy of the system [140–142]. Heat transfer with moving boundary involving phase change is very important in latent heat storage application, i.e., ice formation, freezing of food, castings, metallurgy, crystal growth and various other solidification techniques. The predication of temperature distribution and rate of melting or solidification is very important in order to design such storage device. A number of theoretical efforts were made to study the thermal performance of latent heat storage systems [143–148]. Most of the work maintained was restricted to study the moving boundary problem for specific conditions and designs. None of the author predicted and compares the melt fraction values with time for a latent heat storage system with different PCMs for different heat exchanger container materials.

#### 6.2.1. Numerical simulation of the latent heat storage systems

Following assumptions were made to analyze the latent heat storage system:

Thermophysical properties of the PCMs and fin material are independent of temperature. But they are different for solid and liquid phases of PCM.

(a) PCM is initially in solid phase.
(b) PCM is homogeneous and isotropic.
(c) The mode of heat transfer is conduction only.

#### 6.2.2. Enthalpy formulation

By introducing an enthalpy method, the phase change problem becomes much simpler and has the following advantages: (i) the governing equation is similar to the single phase equation; (ii) there is no condition to be satisfied at the solid–liquid interface as it automatically obeys the interface condition and (iii) the enthalpy formulation allows a mushy zone between the two phases. Phase change problems are usually solved with finite difference or finite element methods in accordance with the numerical approach. The enthalpy formulation is one of the most popular fixed-domain methods for solving the Stefan problem. The major advantage is that the method does not require explicit treatment of the moving boundary. To introduce the formulation, we define an enthalpy function $h$ as a function of temperature and equations are applied over the whole fixed domain as given by Voller [149].

For a phase change process involving either melting or freezing, energy conservation can be expressed in terms of total volumetric enthalpy and temperature for constant thermo-physical properties, as follows:

$$\frac{\partial H}{\partial t} = \nabla(k_k(\nabla T)) \tag{9}$$

where $H$ is the total volumetric enthalpy. It is the sum of sensible and latent heat of the PCM, i.e.

$$H(T) = h(T) + \rho_l f(T)\lambda \tag{10}$$

Here

$$h = \int_{T_m}^{T} \rho_k c_k \, dT \tag{11}$$

In case of isothermal phase change, the liquid fraction of melt is given by

$$f = \begin{cases} 0, & \text{if } T < T_m \quad \text{(solid)} \\ 0-1, & \text{if } T = T_m \quad \text{(mushy)} \\ 1, & \text{if } T > T_m \quad \text{(liquid)} \end{cases} \tag{12}$$

Following Eqs. (10) and (11), the enthalpy of PCM is

$$H = \int_{T_m}^{T} \rho_s c_s \, dT, \qquad T < T_m \quad \text{(solid)} \tag{13a}$$

$$H = \rho_l f \lambda, \qquad T = T_m \quad \text{(melting)} \tag{13b}$$

$$H = \int_{T_m}^{T} \rho_l c_l dT + \rho_l \lambda, \qquad T > T_m \quad \text{(liquid)} \tag{13c}$$

Eq. (13a) represents the sensible enthalpy from the initial temperature ($T_{init}$) to the melting temperature ($T_m$). Solving Eq. (13) for the PCM temperature, one gets

$$T = \frac{T_m + H}{\rho_s c_s}, \quad H < 0 \quad \text{(solid)} \tag{14a}$$

$$T = T_m, \quad 0 \le H \le \rho_l \lambda \quad \text{(interface)} \tag{14b}$$

$$T = \frac{T_m + (H - \rho_l \lambda)}{\rho_l c_l}, \quad H > \rho_l \lambda \quad \text{(liquid)} \tag{14c}$$

Using Eqs. (10) and (11), an alternative form of Eq. (9) for two-dimensional heat transfer in the PCM can be obtained as

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(\alpha \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(\alpha \frac{\partial h}{\partial y}\right) - \rho_l \lambda \frac{\partial f}{\partial t} \tag{15a}$$

and for the heat exchanger container material is

$$\frac{\partial h_f}{\partial t} = \frac{\partial}{\partial x}\left(\alpha_f \frac{\partial h_f}{\partial x}\right) + \frac{\partial}{\partial y}\left(\alpha_f \frac{\partial h_f}{\partial y}\right) \tag{15b}$$

### 6.2.3. Numerical solution

In order to obtain the algebraic equations using the control volume technique developed by Voller [149] and Patankar [150], it was necessary to divide the domain into elementary control volumes and then integrate the equation in these control volumes. Eq. (15a) is solved using a fully implicit finite difference solution method. The finite difference equation for the PCM is obtained on integrating Eq. (15a) over each control volume. The discretization of Eq. (15a) for $\Delta x = \Delta y$ leads to the following scheme (Fig. 24):

$$h_P = h_P^\circ + \alpha R[h_E - 4h_P + h_W + h_N + h_S] + \rho_l \lambda [f_P^\circ - f_P^k] \tag{16}$$

$$a_E h_E + a_W h_W + a_P h_P + a_N h_N + a_S h_S = Q \tag{17}$$

where

$$a_E = a_W = a_N = a_S = -\alpha R,$$

$$a_P = 1 - a_E - a_W - a_P - a_N - a_S$$

and

$$Q = h_P^\circ + \rho_l \lambda [f_P^\circ - f_P^k], \quad R = \frac{dt}{(dx)^2}$$

Eq. (17) has been solved using a tri-diagonal matrix algorithm (TDMA). The central feature of the present fixed grid enthalpy method is the source term $Q$. Here, $h_P^\circ$ and $f_P^\circ$ refer to the enthalpy and the melt fraction, respectively, from the previous time step. The source term $Q$ keeps track of the latent heat evolution, and its driving element is the melt fraction. Its value is determined iteratively from the solution of the enthalpy equation. Hence, after the $(k+1)$th numerical solution of the enthalpy equation of the $P$th node, Eq. (17) may be rearranged as

$$a_P h_P = -a_E h_E - a_W h_W - a_N h_N - a_S h_S + h_P^\circ + \rho_l \lambda [f_P^\circ - f_P^k] \tag{18}$$

If phase change is occurring about the $P$th node (i.e. $0 \le f \le l$), the $(k+1)$th estimate of the melt fraction needs to be updated such that the left side of Eq. (18) is zero, i.e

$$0 = -a_E h_E - a_W h_W - a_N h_N - a_S h_S + h_P^\circ + \rho_l \lambda [f_P^\circ - f_P^{k+1}] \tag{19}$$

Eq. (19) may be rearranged as

$$f_P^{k+1} = \frac{-a_E h_E - a_W h_W - a_N h_N - a_S h_S + h_P^\circ}{\rho_l \lambda + f_P^\circ} \tag{20}$$

The melt fraction update Eq. (20) is applied at every node after the $(k+1)$th solution of Eq. (17) for sensible volumetric enthalpy ($h$), along with under/over correction, i.e.

$$f = \begin{cases} 0, & \text{if } (f)^{k+1} \le 0 \\ 1, & \text{if } (f)^{k+1} \ge 1 \end{cases}$$

Further details concerning the numerical implementation of the present enthalpy method may be found in the work of Costa et al. [137]. Convergence at a given time step is declared when the difference in the total enthalpy fields falls below a given tolerance, i.e.

$$\frac{\mathrm{ABS}[(\mathrm{H}) - (\mathrm{H})]}{\rho_k c_k} < \mathrm{TOL} \tag{21}$$

For the present case, the value of TOL is set to $10^{-4}$. Boundary and initial conditions in the program are the same as given by Costa et al. [137].

Sharma et al. [151], Chen and Sharma [152], Chen et al. [153] developed a two-dimensional theoretical model based on the enthalpy formulation to predict the melting interface profile of the PCMs. The thermophysical properties of various heat exchanger materials [154] are given in

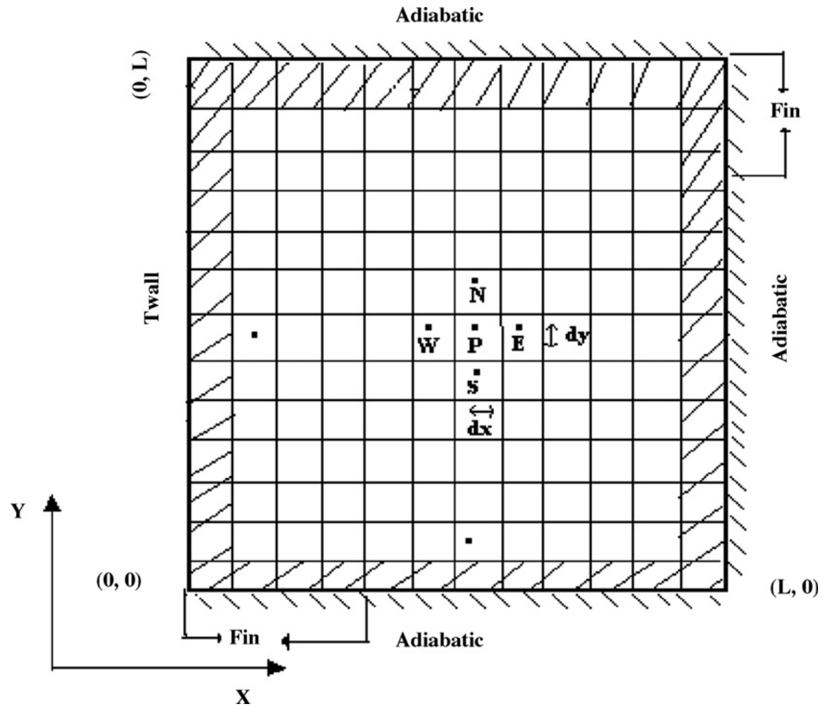



Fig. 24. Two-dimensional domain.

Table 8
Thermophysical properties of various container materials

| Name of material | Thermal conductivity (W/m °C) | Density (kg/m$^3$) | Specific heat (kJ/kg °C) |
|---|---|---|---|
| Glass | 0.78 | 2700 | 0.840 |
| Stainless steel | 7.7 | 8010 | 0.500 |
| Tin | 64 | 7304 | 0.226 |
| Aluminum mixed | 137 | 2659 | 0.867 |
| Aluminum | 204 | 2707 | 0.896 |
| Copper | 386 | 8954 | 0.383 |

Table 8. In order to analyze the performance of the PCM storage system, author considers the effect of thermophysical properties of the PCMs during the melting process on the melt fraction. A grid level of 32 × 32 (2 mm × 2 mm) with time step 20 s has been used where the grid level for the PCM was 30 × 30. The PCMs were assumed 5 °C less than the melting temperature and the heating wall temperature was fixed at 15 °C higher than the melting temperature. Calculations were made to study the effect of thermophysical properties of different PCMs with different type of the heat exchanger container materials on the performance of the latent heat storage system and all results are given in Table 9. Sharma et al. [155] also conducted to study the effects of thermo physical properties on heat exchanger materials on the thermal performance of the storage system. Numerical results show that thermal conductivity, specific heat and density of the heat exchanger container materials increases, the time taken for melting of the phase change material (PCM) decreases. The conclusions of the above reference on the melt fraction thought the enthalpy modeling are given below:

(1) The selection of the thermal conductivity of the heat exchanger container material and effective thermal conductivity of the PCM also very important as these parameters has effect on the melt fraction.
(2) As the thermal conductivity of container material increases, time required for complete melting of the PCM decreases.
(3) Effect of thickness of heat exchanger container material on melt fraction is in-significant
(4) The initial PCM temperature does not have very important effect on the melt fraction, while the boundary wall temperature plays an important role during the melting process and has a strong effect on the melt fraction.

Finally, from the theoretical results it can be concluded for the latent heat storage system, the design parameter of the heat exchanger container materials should be selected carefully in order to optimize the performance of the storage system. The higher value of thermal conductivity of the container material did not make significant contribution on the melt fraction except for at very low thermal conductivities.

Table 9
Melt fraction of the PCMs with various container materials within 300 min (thickness = 2 mm, $T_m - T_{init} = 5\ ^\circ C$, $T_{wall} - T_m = 15\ ^\circ C$)

| Materials | Capric acid | | Lauric acid | | Myristic acid | | Palmitic acid | | Stearic acid | | $CaCl_2 \cdot 6H_2O$ | | $Na_2SO_4 \cdot 10H_2O$ | | N-Octadecane | | Paraffin wax | | $Mg(NO_3)_2 \cdot 6H_2O$ | | Acetamide | | Acetanilide | | Erythritol | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ | $t^*$ | $f$ |
| Glass | 300 | 0.47 | 300 | 0.43 | 300 | 0.41 | 300 | 0.40 | 300 | 0.41 | 300 | 0.45 | 300 | 0.39 | 300 | 0.46 | 300 | 0.66 | 300 | 0.57 | 300 | 0.77 | 300 | 0.80 | 300 | 0.39 |
| Stainless steel | 300 | 0.87 | 300 | 0.80 | 300 | 0.78 | 300 | 0.77 | 300 | 0.77 | 300 | 0.76 | 300 | 0.72 | 300 | 0.83 | 260 | 1.00 | 300 | 1.00 | 202 | 1.00 | 184 | 1.00 | 300 | 0.73 |
| Tin | 300 | 0.98 | 300 | 0.92 | 300 | 0.90 | 300 | 0.89 | 300 | 0.90 | 300 | 0.94 | 300 | 0.88 | 300 | 0.95 | 183 | 1.00 | 235 | 1.00 | 139 | 1.00 | 127 | 1.00 | 300 | 0.85 |
| Aluminum mixed | 246 | 1.00 | 300 | 1.00 | 300 | 1.00 | 300 | 0.98 | 300 | 0.99 | 264 | 1.00 | 300 | 0.98 | 265 | 1.00 | 129 | 1.00 | 165 | 1.00 | 93 | 1.00 | 86 | 1.00 | 300 | 0.96 |
| Aluminum | 230 | 1.00 | 282 | 1.00 | 300 | 1.00 | 300 | 1.00 | 294 | 1.00 | 242 | 1.00 | 300 | 1.00 | 248 | 1.00 | 119 | 1.00 | 153 | 1.00 | 85 | 1.00 | 78 | 1.00 | 300 | 0.98 |
| Copper | 169 | 1.00 | 207 | 1.00 | 220 | 1.00 | 230 | 1.00 | 215 | 1.00 | 172 | 1.00 | 223 | 1.00 | 181 | 1.00 | 87 | 1.00 | 110 | 1.00 | 60 | 1.00 | 55 | 1.00 | 243 | 1.00 |

## 7. Conclusion

This review paper is focused on the available thermal energy storage technology with PCMs with different applications. Those technologies is very beneficial for the humans and as well as for the energy conservation. This paper presents the current research in this particular field, with the main focus being on the assessment of the thermal properties of various PCMs. The heat storage applications used as a part of solar water-heating systems, solar air heating systems, solar cooking, solar green house, space heating and cooling application for buildings, off-peak electricity storage systems, waste heat recovery systems. That paper also presents the melt fraction studies of the few identified PCMs used in various applications for storage systems with different heat exchanger container materials.

## References

[1] Garg HP, Mullick SC, Bhargava AK. Solar thermal energy storage. D. Reidel Publishing Co; 1985.

[2] Project Report. Energy conservation through thermal energy storage. An AICTE project.

[3] Khartchenko NV. Advanced energy systems. Berlin: Institute of Energy Engineering & Technology University; 1997.

[4] Baylin F. Low temperature thermal energy storage: a state of the art survey. Report no. SERI/RR/-54-164. Golden, Colorado, USA: Solar Energy Research Institute; 1979.

[5] Lane GA. Solar heat storage—latent heat materials, vol. I. Boca Raton, FL: CRC Press, Inc.; 1983.

[6] Pillai KK, Brinkwarth BJ. The storage of low grade thermal energy using phase change materials. Appl Energy 1976;2:205–16.

[7] Abhat A. Low temperature latent heat thermal energy storage. In: Beghi C, editor. Thermal energy storage. Dordrect, Holland: D. Reidel Publication Co.; 1981.

[8] Abhat A. Low temperature latent heat thermal energy storage: heat storage materials. Solar Energy 1981;30(4):313–32.

[9] Buddhi D, Sawhney RL.In: Proceedings on thermal energy storage and energy conversion; 1994.

[10] Hale DV, Hoover MJ, O'Neill MJ. Phase change materials hand book. Alabaa: Marshal Space Flight Center; 1971.

[11] Abhat A, et al., Development of a modular heat exchanger with an integrated latent heat storage. Report no. BMFT FBT 81-050. Germany Ministry of Science and Technology Bonn; 1981.

[12] Lane GA, Glew DN. Heat of fusion system for solar energy storage. In: Proceedings of the workshop on solar energy storage subsystems for the heating and cooling of buildings. Virginia: Charlothensville; 1975. p. 43–55.

[13] Herrick S, Golibersuch DC. Quantitative behavior of a new latent heat storage device for solar heating/cooling systems. In: General International Solar Energy Society Conference; 1978.

[14] Lane G.A. et al. Macro-encapsulation of PCM. Report no. ORO/5117-8. Midland, Michigan: Dow Chemical Company; 1978. p. 152.

[15] Lane GA, Rossow HE. Encapsulation of heat of fusion storage materials. In: Proceedings of the second south eastern conference on application of solar energy; 1976. p. 442–55.

[16] Telkes M. Thermal storage for solar heating and cooling. In: Proceedings of the workshop on solar energy storage sub-systems for heating and cooling of buildings. University of Virginia, Charlottesville; 1975.

[17] Biswas R. Thermal storage using sodium sulfate decahydrate and water. Solar Energy 1977;99:99–100.

[18] Charlsson B, Stymme H, Wattermark G. An incongruent heat of fusion system $CaCl_2 \cdot 6H_2O$ made congruent through modification of chemical composition of the system. Solar Energy 1979;23:333–50.

[19] Alexiades V, Solomon Alan D. Mathematical modeling of melting and freezing process. Washington, DC: Hemisphere Publishing Corporation; 1992.
[20] Furbo S. Heat storage units using a salt hydrate as storage medium based on the extra water principle. Report no. 116. Technical University of Denmark; 1982.
[21] Herrick S. A rolling cylinder latent heat storage device for solar heating/cooling. ASHRAE Tans 1979;85:512–5.
[22] George A. Hand book of thermal design. In: Guyer C, editor. Phase change thermal storage materials. McGraw Hill Book Co.; 1989 [chapter 1].
[23] Gustafsson Mari, Bo He, Setterwall Fredrik. Paraffin waxes and their mixture as phase change materials (PCMs) for cool storage in district cooling system. IEA Annex Turkey 1998;10:45–56.
[24] Buddhi D, Sawhney RL, Seghal PN, Bansal NK. A simplification of the differential thermal analysis method to determine the latent heat of fusion of phase change materials. J Phys D Appl Phys 1987;20:1601–5.
[25] Tanishita, Int Solar Energy Eng, Meibourne, Paper 2/73; 1970.
[26] Richards SJ, Chinnery DNW. 42, CSIR Res Rep. 237, South; 1967.
[27] Prakash J, Garg HP, Datta G. A solar water heater with a built-in latent heat storage. Energy Convers Manage 1985;25(1):51–6.
[28] Bansal NK, Buddhi D. An analytical study of a latent heat storage system in a cylinder. Solar Energy 1992;33(4):235–42.
[29] Chaurasia PBL. Phase change material in solar water heater storage system. In: Proceedings of the 8th international conference on thermal energy storage; 2000.
[30] Ghoneim AA. Comparison of theoretical models of phase change and sensible heat storage for air and water solar heating systems. Solar Energy 1989;42(3):209–30.
[31] Bajnoczy G, et al. Heat storage by two grade phase change material. Periodica Polytecinica Ser Chem Eng 1999;43(2):137–47.
[32] Kayugz K, et al. Experimental and theoretical investigation of latent heat storage for water based solar heating systems. Energy Convers Manage 1995;36(5):315–23.
[33] Rabin Y, Bar-Niv I, Korin E, Mikic B. Integrated solar collector storage system based on a salt hydrate phase change material. Solar Energy 1995;55(6):435–44.
[34] Sharma A, Sharma A, Pradhan N, Kumar B. Performance evaluation of a solar water heater having built in latent heat storage unit, IEA, ECESIA Annex 17. Advanced thermal energy storage through phase change materials and chemical reactions—feasibility studies and demonstration projects. 4th workshop, Indore, India. March 21–24, 2003; p. 109–15.
[35] Mettawee E-BS, Assassa GMR. Experimental study of a compact PCM solar collector. Energy 2006;31:2958–68.
[36] Cabeza LF, Ibanez M, Sole C, Roca J, Nogues M. Experimentation with a water tank including a PCM module. Solar Energy Mater Solar Cells 2006;90:1273–82.
[37] Canbazoglu S, Şahinaslan A, Ekmekyapar A, Gokhan Aksoy Y, Akarsu F. Enhancement of solar thermal energy storage performance using sodium thiosulfate pentahydrate of a conventional solar water-heating system. Energy Build 2005;37:235–42.
[38] Morrison DJ, Abdel Khalik SI. Effects of phase change energy storage on the performance of air-based and liquid-based solar heating systems. Solar Energy 1978;20:57–67.
[39] Jurinak JJ, Adbel Khalik SI. On the performance of air-based solar heating systems utilizing phase change energy storage. Solar Energy 1979;24:503–22.
[40] Ghoneim AA, Klein SA. The effect of phase change material properties on the performance of solar air-based heating systems. Solar Energy 1989;42(6):441–7.
[41] Enibe SO. Performance of a natural circulation solar air heating system with phase change material energy storage. Renew Energy 2002;27:69–86.
[42] Zhou G, Zhang Y, Zhang Q, Lin K, Di H. Performance of a hybrid heating system with thermal storage using shape-stabilized phase-change material plates. Appl Energy 2007;84(10):1068–77.
[43] Domanski. et al. Cooking during off sunshine hours using PCMs as storage media. Fuel Energy Abstr 1995;36(5):348.
[44] Buddhi D, Sahoo LK. Solar cooker with latent heat storage design and experimental testing. Energy Convers Manage 1997;38(5):493–8.
[45] Sharma SD, Buddhi D, Sawhney RL, Sharma A. Design, development and performance evaluation of a latent heat unit for evening cooking in a solar cooker. Energy Convers Manage 1997;38(5):493–8.
[46] Buddhi D, Sharma SD, Sharma A. Thermal performance evaluation of a latent heat storage unit for late evening cooking in a solar cooker having three reflectors. Energy Convers Manage 2003;44(6):809–17.
[47] Sharma SD, Iwata T, Kitano H, Sagara K. Thermal performance of a solar cooker based on an evacuated tube solar collector with a PCM storage unit. Solar Energy 2005;78:416–26.
[48] Hung K, Abrams CF, Jr., Coasts LL, Bowers CG. Jr., Development of greenhouse bulk drying systems for solar energy utilization and planted mechanization. AHARE paper no. 75-1018, Am. Soc. Agric. Eng., St. Joseph, MI; 1975.
[49] Kern M, Aldrich RA. Phase change energy storage in a greenhouse solar heating system. ASME paper no. 79-4028. Am Soc. Agric. Eng., St. Joseph, MI; 1979.
[50] Hung K, Toksoy M. Design and analysis of green house solar system in agricultural production. Energy Agric 1983;2(2):115–36.
[51] Hhyum – Kasp Song, Utilization of latent heat storage materials for the high concentrated thermal energy storage. Report no. 1988.5–19990.5; 1988.
[52] Nishina H, Takakura T. Greenhouse heating by means of latent heat storage units. Acta Hort (Energy in Protected Cultivation Ill) 1984;148:751–4.
[53] Takakura T, Nishina H. A solar greenhouse with phase change energy storage and a microcomputer control system. Acta Hort (Energy in Protected Cultivation) 1981;115:583–90.
[54] Baille A, Boulard T. Phase change material for heat storage in greenhouse. In: von Zabeltitz C, editor. REUR technical series l—greenhouse heating with solar energy. CNRE; 1987. p. 139–42.
[55] Boulard T, Razafinjohany E, Baille A, Jaffrin A, Fabre B. Performance of a greenhouse heating system with a phase change material. Agric Forest Meteorol 1990;52:303–18.
[56] Huseyin Ozturk H. Experimental evaluation of energy and exergy efficiency of a seasonal latent heat storage system for greenhouse heating. Energy Convers Manage 2005;46:1523–42.
[57] Swet J. Phase change storage in passive solar architecture. In: Proceedings of the 5th national passive solar conference. Massachusetts: Amhearst; 1980. p. 282–6.
[58] Ghoneim AA, Klein SA, Duffie JA. Analysis of collector–storage building walls using phase change materials. Solar Energy 1991;47(1):237–42.
[59] Eiamworawutthikul C, Strohbehn J, Harman C. Investigation of phase-change thermal storage in passive solar design for light-construction building in the southeastern climate region. A research program to promote energy conservation and the use of renewable energy. http://intraweb.stockton.edu/eyos/energy_studies/content/docs/FINAL_PAPERS/14B-1.pdf.
[60] Bourdeau LE. Study of two passive solar systems containing phase change materials for thermal storage. In: Hayes J, Snyder R, editors. Proceedings of fifth national passive solar conference, October 19–26, Amherst. Newark, Delaware: American Solar Energy Society; 1980. p. 297–301.
[61] Swet CJ. Phase change storage in passive solar architecture. In: Proceedings of the 5th national passive solar conference; 1980. p. 282–6.
[62] Ghoneim AA, Kllein SA, Duffie JA. Analysis of collector–storage building walls using phase change materials. Solar Energy 1991;47(1):237–42.
[63] Chandra S, Kumar R, Kaushik S, Kaul S. Thermal performance of a non A/C building with PCCM thermal storage wall. Energy Convers Manage 1985;25(1):15–20.
[64] Knowler T. Proportioning composites for efficient-TSWs. Solar Energy 1983;31(3):319–26.
[65] Stritih U., Novak P., Solar heat storage wall for building ventilation. World renewable energy congress (WREC); 1996. p. 268–71.
[66] Kedl RJ, Stovall TK, Activities in support of the wax-impregnated wallboard concept. Thermal energy storage researches activity review. New Oreleans, Louisiana, USA: US Department of Energy; 1989.

[67] Salyer IO, Sircar AK. Phase change material for heating and cooling of residential buildings and other applications. In: Proceedings of 25th intersociety energy conservation engineering conference; 1990. p. 236–43.
[68] Shapiro MM, Feldman D, Hawes D, Banu D. PCM thermal storage in wallboard. In: Proceedings 12th passive solar conference, Portland; 1987. p. 48–58.
[69] Shapiro M. Development of the enthalpy storage materials, mixture of methyl stearate and methyl palmitate. Subcontract report to Florida Solar Energy Center; 1989.
[70] Feldman D, Khan MA, Banu D. Energy storage composite with an organic phase change material. Solar Energy Mater 1989;18:333–41.
[71] Feldman D, Shapiro M, Banu D, Fuks CJ. Fatty acids and their mixtures as phase change materials for thermal energy storage. Solar Energy Mater 1989;18:201–16.
[72] Feldman D, Banu D, Hawes D, Ghanbari E. Obtaining an energy storing building material by direct incorporation of an organic phase change material in gypsum wallboard. Solar Energy Mater 1991;22:231–42.
[73] Hawes DW, Feldman D, Banu D. Latent heat storage in building materials. Energy Build 1993;20:77–86.
[74] Neeper DA. Solar buildings research: what are the best directions? Passive Solar J 1986;3:213–9.
[75] Neeper DA. Potential benefits of distributed PCM thermal storage. In: Coleman MJ, editor. Proceedings 14th national passive solar conference, June 19–22, Denver, Colorado. American Solar Energy Society; 1989 p. 283–8.
[76] Neeper DA. Thermal dynamics of wallboard with latent heat storage. Solar Energy 2000;68:393–403.
[77] Stovall TK, Tomlinson JJ. What are the potential benefits of including latent heat storage in common wall board. Trans ASME 1995;117: 318–25.
[78] Drake JB. A study of the optimal transition temperature of PCM wallboard for solar energy storage. Oak Ridge National Laboratory report ORNL/TM-10210 available from National Technical Information Service. 5285 Port Royal Road, Springfield, VA 2161, USA; 1987.
[79] Peippo K, Kauranen P, Lund PD. A multi-component pcm wall optimized for passive solar heating. Energy Build 1991;17:259–70.
[80] Stetiu C, Feustel HE. Phase change wallboard as an alternative to compressor cooling in californian residences. In: Proceedings of 96 ACEE summer study for energy efficient building; 1996.
[81] Athienitis AK, Liu C, Hawes D, Banu D, Feldman D. Investigation of the thermal performance of a passive solar test-room with wall latent heat storage. Build Environ 1997;32:405–10.
[82] Kisssock JK, Hamming JM, Whitney TI, Drake ML. Testing and simulation of phase change wallboard for thermal storage in buildings. In: Proceedings of international solar energy conference; 1998. p. 45–52.
[83] Kalousck M, Hirs J. Simulation of the summer indoor thermal comfort by using wallboard with phase change material. Bologna: Eurosun; 2002.
[84] Schossig P, Henning H-M, Gschwander S, Haussmann T. Micro-encapsulated phase-change materials integrated into construction materials. Solar Energy Mater Solar Cells 2005;89:297–306.
[85] Harald Mehling: strategic project "Innovative PCM-Technology"—results and future perspectives. 8th expert meeting and work shop, Kizkalesi, Turkey, April 18–20, 2004.
[86] Athienities A, Chen Y. The effect of solar radiation on dynamic thermal performance of floor heating systems. Solar Energy 2000;69(3):229–37.
[87] Bakos G. Energy management method for auxiliary energy saving in a passive-solar-heated residence using low-cost off-peak electricity. Energy Build 2000;31(3):237–41.
[88] Lin KP, Zhang YP, Xu X, Di HF, Yang R, Qin PH. Modeling and simulation of under-floor electric heating system with shapestabilized PCM plates. Build Environ 2004;39(12):1427–34.
[89] Nagano K, Mochida T, Iwata K, Hiroyoshi H, Domanski R, Rebow M. Development of new PCM for TES of the cooling system, Terrastock. In: Benner M, Hahne EWP, editors. 8th International Conference on Thermal Energy Storage. 2000.p. 345–50.
[90] Frank B. Phase change material for space heating and cooling. Sustainable Energy Center: University of South Australia; Presentation 2002.
[91] Benard C, Gobin D, Gutierrez M. Experimental results of a latent heat solar roof used for breeding chickens. Solar Energy 1981;6(4): 347–54.
[92] Gutherz JM, Schiler ME. A passive solar heating system for the perimeter zone of office buildings. Energy Sources 1991;13:39–54.
[93] Turnpenny JR, Etheridge DW, Reay DA. Noval ventilation cooling system for reducing air conditioning in buildings. Part I. Testing and theoretical modeling. Appl Therm Eng 2000;20:1019–37.
[94] Kodo T, Ibamoto T. Research on using the PCM for ceiling board, IEA ECESIA, Annex 17, 3rd workshop, Tokyo, Japan. October 1–2, 2002.
[95] Telkes M. Solar energy storage. Am Soc Heat Refrig Air Cond Eng 1974;38–44.
[96] Herrick S, Thermal energy storage subsystem for solar heating and cooling applications. Paper presented at third annual energy storage concentrator's information exchange meeting. Springfield, VA, December 5–6, 1978.
[97] Gawarn K, Scroder J. Properties of some salt hydrates for latent heat storage. Energy Res 1977;1:351.
[98] Lane GA, et al. Heat of fusion systems for solar energy storage. In: Proceedings of the workshop solar energy storage subsystems for the heating and cooling of buildings; 1975. p. 43–55.
[99] Buddhi D. et al., Annual progress report. 'Peak reduction of air conditioning systems through thermal storage', A DAE project, funded by Bhabha Atomic Research Center, Govt. of India at School of Energy & Environmental Studies, Devi Ahilya University, Indore 17, India; 2001.
[100] Arimatsu I, Kawahara T, Hamatani M, Hamako Y. Nat Tech Rep 1971;17:155.
[101] Lillich KH. Electro–Tech 1971;49:579.
[102] Shitzer, Levy M. Trans ASME J Sol Energy Eng 1983;105:200.
[103] Farid MM, Husian Rafah M. An electrical storage heater using the phase change method of heat storage. Energy Convers Manage 1990;30(3): 219–30.
[104] Brandstetter A, Kaneff S. Materials and systems for phase change thermal storage. In: Proceedings of the Ist world renewable energy congress; 1990. p. 1460–4.
[105] Farid MM, Husain RF. An electrical storage heater using the phase change method of heat storage. Energy Convers Manage 1990;30(3): 219–30.
[106] Theunissen PH, Buchlin JM. Numerical optimization of a solar air heating system based on encapsulated PCM storage. Solar Energy 1983;31(3):271–7.
[107] Farid MM, Chen XD. Domestic electrical space heating with heat storage. Proc Inst Mech Eng 1999;213:83–92.
[108] Buddhi D. Thermal performance of a shell and tube PCM storage heat exchanger for industrial waste heat recovery. Presented at solar world congress, Taejon, Korea, August 24–30, 1977.
[109] Abhat A. Performance studies of a finned heat pipe latent heat thermal energy storage system. Sun, NY: Pergamon Press; 1981. pp. 541–546.
[110] Maccracken CD. PCM bulk storage. In: Proceedings of the international conference on energy storage; 1981. p. 159–65.
[111] Smith RN, Ebersole TE, Griffin FP. Solar Energy Eng 1980;102:112.
[112] Morcos VH. Investigation of a latent heat thermal energy storage system. Solar Wind Technol 1990;7(2/3):197–202.
[113] Cho et al. Heat transfer in a latent heat storage system using $MgCl_2 \cdot 6H_2O$ at the melting point. Paper no. 1393/27.
[114] Herrick CS. Multi-freeze cycle life testing of Glauber's salt in a rolling cylinder heat store. Solar Energy 1982;28:99.
[115] Santamouris MJ, Lefas CC. On the coupling of PCM stores to active solar systems. Int J Energy Res 1988;12:603–10.
[116] Bouriotis V, Santamouris MJ, Lefas CC. Architectural design, thermal performance and operational strategies of a hybrid solar building in Athens, Greece. In: Proceedings of the 2nd solar energy Arab conference; 1986.
[117] Farid MM, Kanzawa A. Thermal performance of heat storage module using PCMs with different melting temperatures: mathematical modeling. Trans ASME J Solar Energy Eng 1989;111:152–7.
[118] Stefan J. Uber einge problem der theoric der warmeleitung, S. B. Wein, Acad. Mat. Natur. 1989;98:173–484.

[119] Carslaw HS, Jager JC. Conduction of heat in solids, 2nd ed., London: Oxford University Press; 1973.
[120] Lauardini VJ. Heat transfer in cold climates. New York: Pub. Van Nostrand; 1981.
[121] Goodman TR. The heat balance integral and its application in problems involving a change. Trans ASME 1958;80:335–42.
[122] Yeh LT, Chung BT. Solidification and melting of material subjected to convention and radiation. J Space Cr Rockets 1975;12:329–34.
[123] Crank J, Gupta R. Isothermal migration in two dimensions. Int J Heat Mass Transfer 1975;18:1101–17.
[124] Keung CS. The use of sources and sinks in solving two dimension conduction problem with change of phase in arbitrary domains. Ph.D. dissertation, Columbia University, New York, 1980.
[125] Buddhi D, et al. Solar thermal storage systems using phase change materials. Int J Energy Res 1988;12:547–55.
[126] Lazaridas. A numerical solution of the multidimensional solidification (or melting) problem. Int J Heat Mass Transfer 1970;13:1459–77.
[127] Bonacina. et al. Numerical solution phase change problems. Int J Heat Mass transfer 1973;16:1825–32.
[128] Comini. et al. Finite element solution of non-linear heat conduction with phase changes. Int J Numer Methods Eng 1970;8:613–24.
[129] Rolph III W, Bathe KJ. An efficient algorithm for analysis of nonlinear heat transfer with phase change. Int J Numer Methods Eng 1982;18: 119–34.
[130] Hsiao JS, Chung BTF. An efficient algorithm for finite solution to two dimensional heat transfer with melting and freezing. ASME paper 84-HT-2. Presented at the 22nd national heat transfer conference, Niagara Falls, August 1984.
[131] Yoo J, Rubinsky B. Numerical computation using finite elements for the moving interface in heat transfer problems with phase change transformation. Numer Heat Transfer 1983;6:209–22.
[132] Bounerot R, Janet P. Numerical computation of free boundary for the two dimensional Stefan problems by space–time finite elements. J Comput Phys 1977;25:163–81.
[133] Wu S, Ruo K, Algilhers L. On the ADI scheme for the two dimensional transient heat conduction problem with phase change. AIAA paper AIAA-84-0395; 1984.
[134] Shamsunder N, Sparrow E. Analysis of multidimensional phase change via the enthalpy model. J Heat Transfer Trans ASME 1975;19:333–40.
[135] Hibbert SE, Markatos NC, Voller VR. Computer simulation of moving interface, convective, phase change process. Int J Heat Mass Transfer 1988;31:1785–95.
[136] Comini G, et al. Finite element of non-linear heat conduction problems with special reference to phase change. Int J Number Meth Eng 1974;8: 613–24.
[137] Costa M, Buddhi D, Oliva A. Numerical simulation of a latent heat thermal energy storage system with enhanced heat conduction. Energy Convers Manage 1998;39(3/4):319–30.
[138] Dalhuijsen AJ, Segal A. Comparison of finite element techniques for conduction problems. Int J Numer Meth Eng 1986;23:1807–29.
[139] Wen, Sheffled JW, O'Dell MP. Analytical and experimental investigation of melting heat transfer. J Thermophys 1989;3:330–9.
[140] Swaminathan CR, Vollar VR. On the enthalpy method. Int J Num Meth Heat Fluid Flow 1993;3:233–44.
[141] Vollar VR, et al. An enthalpy method for convection, fusion phase change. Int J Numer Meth Eng 1987;24:271–84.
[142] Alexiades V, Solomon AD. Mathematical modeling of melting and freezing processes. USA: Hemisphere Publishing Corporation; 1993.
[143] Laoud A, Lacroix M. Thermal performance of a latent heat energy storage ventilated panel for electric load management. Int J Heat Mass Transfer 1999;42:275–86.
[144] Bansszek Jerzy, Domanski R, Rebow M, El-Sagier F. Experimental study of solid–liquid phase change in a spiral thermal energy storage unit. Appl Therm Eng 1999;19:1253–77.
[145] Lacroix M. Numerical simulation of a shell and tube latent heat thermal energy storage unit. Solar Energy 1993;50(4):357–67.
[146] Zivkovic B, Fujji I. An analysis of isothermal phase change of phase change material within rectangular and cylindrical containers. Solar Energy 2001;70(1):51–61.
[147] Humphries W, Griggs E. A design handbook for phase change thermal control and energy storage devices. NASA TP-1074; 1977.
[148] Lamberg P, Siren K. Analytical model for melting in semi-infinite PCM storage with an internal fin. Heat Mass Transfer 2003;39:167–76.
[149] Voller VR. Fast implicit finite-difference method for the analysis of phase change problems. Numer Heat Transfer Part B 1990;17:155–69.
[150] Patankar SV. Numerical heat transfer and fluid flow. Washington, DC: Hemisphere Publishing Corporation; 1980.
[151] Sharma A, Won LD, Buddhi D, Park JU. Numerical heat transfer studies of the fatty acids for different heat exchanger materials on the performance of a latent heat storage system. Renew Energy 2005;30(14):2179–87.
[152] Chen CR, Sharma A. Numerical investigation of melt fraction of PCMs in a latent heat storage system. J Eng Appl Sci 2006;1(4):437–44.
[153] Chen CR, Sharma A, Tyagi SK, Buddhi D. Numerical heat transfer studies of PCMs used in a box type solar cooker. Renew Energy; in press.
[154] Garg HP. Treatise on solar energy: fundamentals of solar energy, vol. 1. John Wiley & Sons; 1982.
[155] Sharma A, Sharma SD, Buddhi D, Won LD. Effect of thermo physical properties of heat exchanger material on the performance of latent heat storage system using an enthalpy method. Int J Energy Res 2006;30(3): 191–201.